



# SAMPLING AND ANALYSIS OF CARBON AND ALLOY STEELS

METHODS OF THE CHEMISTS OF  
THE SUBSIDIARY COMPANIES OF  
THE UNITED STATES STEEL COR-  
PORATION AS REVISED TO 1937.

*BOOK DEPARTMENT*

REINHOLD PUBLISHING CORPORATION  
330 WEST FORTY-SECOND STREET, NEW YORK, U. S. A.

1938



COPYRIGHT 1938 BY  
REINHOLD PUBLISHING CORPORATION

---

*All rights reserved*

*Printed in the United States of America by*  
INTERNATIONAL TEXTBOOK PRESS, SCRANTON, PA.

## Preface

This book replaces two former booklets dealing with the sampling and analysis of plain carbon steels and of alloy steels. The methods described include revisions of the older methods and some newer methods which have been found most practicable and otherwise satisfactory for the purposes to which they are applied. For the most part, the methods are those actually in frequent use by the several laboratories represented on the committee, but include also methods that are seldom required by some laboratories. Much effort has been expended in searching out the best, and the book includes more than two years' coöperative effort of the following committee and others in developing, investigating, and standardizing methods.

Mr. J. V. Freeman, Chairman, Chemists' Committee, United States Steel Corporation of Del., 71 Broadway, New York, New York.

Mr. A. D. Beers, Chief Chemist, alternate, Mr. G. P. Burke, Assistant Chief Chemist, Gary Works, Carnegie-Illinois Steel Corporation, Gary, Indiana

Mr. W. D. Brown, Chief Chemist, Duquesne Works, Carnegie-Illinois Steel Corporation, Duquesne, Pennsylvania

Mr. L. P. Chase, Chief Chemist, South Works, Carnegie-Illinois Steel Corporation, Chicago, Illinois

Mr. C. B. Francis, Chemist and Metallurgist, Bureau of Information and Service Tests, Carnegie-Illinois Steel Corporation, Pittsburgh, Pennsylvania

Mr. W. J. Frederick, Chemist, Research Laboratory, Carnegie-Illinois Steel Corporation, Pittsburgh, Pennsylvania

Mr. S. S. Heide, Chief Chemist, Tennessee Coal, Iron and Railroad Company, Ensley, Alabama

Mr. George A. Hopkins, succeeded by Mr. Carl Ruhe, Chief Chemist, Homestead Works, Carnegie-Illinois Steel Corporation, Munhall, Pennsylvania.

Mr. C. P. Larrabee, Corrosion Research Laboratory, Carnegie-Illinois Steel Corporation, Vandergrift, Pennsylvania

Mr. W. F. Muehlberg, Chief Chemist, Cleveland District Laboratory, American Steel and Wire Company, Cleveland, Ohio

Mr. C. E. Nesbitt, Chief Chemist, Edgar Thomson Works, Carnegie-Illinois Steel Corporation, Braddock, Pennsylvania

Mr. R. J. Ruff, Chief Chemist, Donora Steel Works, American Steel and Wire Company, Donora, Pennsylvania

Mr. P. C. Welter, Chief Chemist, Lorain Works, National Tube Company, Lorain, Ohio

Mr. E. C. Wright, Chief Chemist and Metallurgist, succeeded by Mr. W. M. Davidson, Chief Chemist, Ellwood Works, National Tube Company, Ellwood City, Pennsylvania

Mr. T. S. Woodward, Chief Chemist, Ohio Works, Carnegie-Illinois Steel Corporation, Youngstown, Ohio

Mr. E. L. Bush, Chief Chemist, Vandergrift Works, Carnegie-Illinois Steel Corporation, Vandergrift, Pennsylvania

### Acknowledgements

The committee wishes to acknowledge the assistance of many other chemists of the United States Steel Corporation, who, through their associations, have contributed, from time to time, a great deal to the development of methods recorded in this book. Several have made noteworthy contributions, and are credited in the text. Also, the members are indebted to all those specializing in analytical chemistry who have published the results of their work. Among references found most helpful are the following:

1. "Chemical Analysis of Iron and Steel," by G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, New York, John Wiley & Sons, Inc., 1931.
2. The Journal of the American Chemical Society, Chemical Abstracts, and Industrial and Engineering Chemistry, Analytical Edition, published by the American Chemical Society, Washington, D. C.
3. Methods of the American Society for Testing Materials.
4. Journal of Research of the National Bureau of Standards, Washington, D. C.

# Contents

	<i>Page</i>
<b>Sampling</b>	
PRELIMINARY TESTS .....	19
Sampling: Tests for Drilling; Rapid Methods for.	
SAMPLING UNDER SPECIFICATIONS .....	22
Size of Samples; Marking for Identification.	
THE LADLE TEST .....	23
Sampling; Number of Tests; Procedure; Use of Aluminum to Kill the Test; Mold for Ladle Test Ingot; Marking for Identification; Drilling; Sieving the Cuttings.	
SAMPLING FROM BLOOMS AND BILLETS .....	27
SAMPLING OF FINISHED MILL PRODUCTS .....	28
Number of Samples; Rods, small bars, etc.; Large bars and shapes; Pipes and tubes; Strip; Sheets.	
<b>Qualitative and Quick Tests for Identifying Various Types of Steel</b>	
QUALITATIVE TESTS .....	34
Test Using a Single Sample: Apparatus; Solutions Required: Zinc Chloride, Lead Acetate, Mercuric Chloride Paper; Procedure: Test for Se, S, and As; for Cr; for Si, W, Cb, Ta, Zr; for Ti and V; for Co and Ni; for Molybdenum and Cu; for Zirconium; for Tin.	
QUALITATIVE TESTS USING SEPARATE SAMPLES .....	37
Procedure: Chromium, Vanadium, Titanium, Zirconium, Cobalt.	
QUICK TESTS FOR IDENTIFYING STEELS .....	38
Tests for High-sulphur steels: Arsenic Test; Print Test; Smear Test for Nickel; Quick Test for Ti and V in Stainless Steels: Procedure.	
<b>Methods of Analysis</b>	
GENERAL REMARKS .....	40
Caution in Use of Perchloric Acid; Concentration of Solutions; Use of ml instead of cc; Elements that may occur in steel.	
DETERMINATION OF CARBON, METHODS OF .....	41
COMBUSTION IN OXYGEN .....	43
Introductory Remarks; Limits of Accuracy for Carbon by this Method; Apparatus and Reagents: Oxygen Supply; Pressure Reducing Valves; Oxygen Purifying Train: Mercury Trap or Manometer; Electric Furnace; Rheostat; Pyrometer; Combustion Tube; Boat and Lining; Second Purifying Train; Removal of Dust, SO <sub>2</sub> , etc.; Preparation of Manganese Dioxide; Preparation of Manganese Tower; Desiccants; CO <sub>2</sub> Absorption Bulb; Gas Flow Indicator; Checking the Train; Weight of Sample; Use of Accelerators with Sample; Fineness of Cuttings.	

	<i>Page</i>
GRAVIMETRIC METHOD: DIRECT WEIGHING OF CARBON DIOXIDE	53
GRAVIMETRIC METHOD: WEIGHING CARBON DIOXIDE AS BARIUM CARBONATE.....	54
Procedure; Solutions and Blanks: Barium Hydroxide Solution.	
VOLUMETRIC METHOD TITRATING EXCESS BARIUM HYDROXIDE..	56
Procedure; Solutions Required: Water; Standard HCl Solution; BaOH Solution; Phenolphthalein Solution.	

### Chemical Separations

BICARBONATE SEPARATION.....	59
Elements Separated and Use of the Method; Procedure.	
ZINC OXIDE SEPARATION.....	60
Elements Separated and Use of the Method; Procedure: Zinc Oxide Emulsion.	
LEAD PERCHLORATE SEPARATION OF CHROMIUM IN PRESENCE OF MANGANESE, TITANIUM, VANADIUM, AND ALUMINUM.....	62
Uses of the Method; Special Solutions Required: Lead Perchlorate Solution (0.5 M), Silver Perchlorate Solution (0.5 M); Procedure.	
PERCHLORIC ACID-AMMONIUM PERSULPHATE SEPARATION (FOR MANGANESE).....	64
Elements Separated and Use of the Method; Procedure.	
CHLORATE METHOD FOR ISOLATION OF MANGANESE.....	65
Procedure: Asbestos Filter.	
ETHER SEPARATION.....	66
Uses of the Method and Elements Separated; Procedure: Sample of 5 g; of 10 g; of 2 g.	
SEPARATION WITH CUPFERRON.....	68
Elements Completely Precipitated; Elements Partly Precipitated; Elements that Remain in Solution; Special Reagent Solution; Procedure.	
SEPARATION OF CHROMIUM AS CHROMYL CHLORIDE.....	70
Principles and Application of the Method; Procedure for Solution of Sample and Elimination of Most of the Chromium; Procedure for Eliminating All Chromium; Effect of the Treatment upon other Elements: Tin, Arsenic; Loss of other Elements and Interference of Perchloric Acid.	

### Determination of Manganese

METHODS AND THEIR APPLICATION.....	74
THE PERSULPHATE METHOD.....	74
APPLICATIONS OF THE METHOD TO PLAIN-CARBON AND LOW-ALLOY STEELS.....	75
Procedure I: Visual Titration with Precipitation of Silver Ion; Absence of Chromium or Tungsten; Presence of Chromium or Tungsten, Cr under 5%, Cr over 5%; Procedure II: Visual Titration in Presence of Silver Ion.	

APPLICATION OF THE METHOD TO ALLOY STEELS.....	76
--	----

Treatment of Sample when a Preliminary Separation is not required.

RAPID METHOD FOR HIGH-CHROMIUM, STAINLESS AND HEAT-RESISTANT STEELS .....	77
---	----

Solution of the Sample and Elimination of Chromium; Oxidation of Manganese; Treatment of Sample in the Presence of much Chromium or much Chromium and Tungsten; Treatment of Sample in the Presence of Tungsten with Chromium Absent or Under 1%; Oxidation and Titration of the Manganese; Other Modifications of the Method: The Larrabee Apparatus; Preparation of Sample for Titration; Solutions and Special Reagents Required: Silver Nitrate Solution, Ammonium Persulphate Solution, Standard Sodium Arsenite Solution, Nitric-Sulphuric-Phosphoric Acid Mixture.

SODIUM BISMUTHATE METHOD.....	81
-------------------------------	----

Application of the Method; Weight and Treatment of Sample: Blank; Treatment of Sample in Presence of Cobalt; Treatment of Sample in Presence of Tungsten; Treatment of Sample in Absence of Cobalt and Presence of Much Cr, P, or Ni; Treatment of Sample When a Preliminary Separation is Not Required; Oxidation of the Manganese with Bismuthate: Ferrous Sulphate-Permanganate Titration; Titration with Standard Sodium Arsenite Solution; Solutions and Special Reagents Required: Apparatus; Dilute Nitric Acid (sp. gr. 1.135); Dilute Nitric Acid (3%); Asbestos Filter; Bismuthate; Ferrous Ammonium Sulphate; Standard Solutions of  $\text{KMnO}_4$  and Sodium Arsenite; Oxidation of Manganese in  $\text{H}_2\text{SO}_4$  Solution Followed by Potentiometric Titration.

THE GRAVIMETRIC PHOSPHATE METHOD.....	85
---------------------------------------	----

### Determination of Phosphorus

THE MOLYBDATE METHOD .....	87
----------------------------	----

General Precautions; Solution of Sample and Precipitation of Phosphorus; Weight of Sample.

PROCEDURE FOR DISSOLVING STEELS CONTAINING LITTLE OR NO SILICON, TITANIUM, TUNGSTEN, URANIUM, ZIRCONIUM, COLUMBIUM OR TANTALUM .....	89
--	----

Weight and Solution of Sample; Precipitation of Phosphorus; Treatment of Residues; Treatment of the Yellow Precipitate for Estimation of Phosphorus; Alkalimetric Method, Gravimetric Magnesia Method; Special Solutions Required: Acid Ammonium Molybdate Solution, Ammonium Molybdate, Johnson's Formula, Phenolphthalein Indicator Solution, Acid Magnesia Mixture.

THE ACETATE METHOD.....	97
-------------------------	----

Application of the Method; Special Solution Required: Acid Ammonium Sulphuric Solution.

### Determination of Sulphur

METHODS FOR DETERMINING SULPHUR.....	100
--------------------------------------	-----

VOLUMETRIC EVOLUTION METHOD.....	101
----------------------------------	-----

Ordinary Procedure in Absence of Mo, W, Se, and Zr; also High Percentages of Al and Ti: Application; Procedure.

	<i>Page</i>
<b>SPECIAL PROCEDURES</b> .....	103
Absence of Se and Zr: Use of Concentrated HCl, Hydrofluoric Acid; Se Present, Mo and Zr Absent: Special Solution Required: Acid Zinc- Potassium Chloride; Procedure; Solutions Required: Dilute HCl, Ammoniacal CuSO <sub>4</sub> , Ammoniacal CdCl <sub>2</sub> , Stock NaOH-Starch Solution, Starch Solution, Titrating Solution.	
<b>GRAVIMETRIC METHODS</b> .....	107
Nitric Acid Method: Procedure for Plain-Carbon Steel; Procedures for Tungsten and Low-Sulphur Alloy Steels Insoluble in Nitric Acid; Pro- cedure for Tungsten Steels; Copper-Potassium Chloride or Meineke Method: Special Solution Required; Procedure.	
<b>Determination of Silicon</b>	
<b>METHODS AVAILABLE</b> .....	111
Loss from Soluble Silicon; Weight of Sample.	
<b>METHODS INVOLVING DEHYDRATION OF THE SILICA WITH PER- CHLORIC ACID</b> .....	112
Procedure Applicable to Plain-Carbon Steels: Nitric-Sulphuric Acid Method: Special Solution Required; Procedure Applicable to all Steels except those Containing W and much Cr; Hydrochloric-Sulphuric Acid Method: Solution of Sample and Dehydration of the Silica, Purification of the Silica; Procedure for Tungsten Steels: Procedure A, Separating both Si and W; Procedure B, Separating Si with W.	
<b>Determination of Copper</b>	
<b>OCCURRENCE OF COPPER AND METHODS AVAILABLE</b> .....	116
<b>SOLUTION OF SAMPLE AND SEPARATION OF COPPER WITH HYDRO- GEN SULPHIDE</b> .....	116
Procedure for all steels except those containing W; Procedure for steels containing W.	
<b>SOLUTION OF SAMPLE AND SEPARATION OF COPPER WITH SODIUM THIOSULPHATE</b> .....	117
Procedure in Absence of W: Solution in Oxidizing Mixture, Solution in H <sub>2</sub> SO <sub>4</sub> : Procedure in Presence of W.	
<b>PURIFICATION OF COPPER SULPHATE PRECIPITATE: SEPARATION OF MOLYBDENUM</b> .....	118
NaOH Separation; Alpha-benzoinoxime Separation.	
<b>METHODS FOR DETERMINATION OF COPPER</b> .....	119
Gravimetric CuO Method; Electrolytic Method; KI-Thiosulphate Volumetric Method: Standard Sodium Thiosulphate Solution; Pro- cedure; Colorimetric Method: Procedure.	
<b>THIOCYANATE-IODATE METHOD</b> .....	120
Special Solutions Required: Starch, Potassium Iodide, Potassium Thio- cyanate, Standard Potassium Iodate, Standard Sodium Thiosulphate; Standardization of Solutions; Weight of Sample; Procedure: Carbon and Low-Alloy Steels, High-Chromium Nickel Steels, Steels Containing W; Cr Present or Absent: Separation and Titration of the Copper.	

## Determination of Nickel

	<i>Page</i>
OCCURRENCE OF NICKEL AND METHODS AVAILABLE .....	125
SILVER NITRATE-POTASSIUM CYANIDE TITRATION METHOD .....	125
Application of the Method; Weight of Sample; Blanks; Solution of Sample: Cr Absent or Low, Cu, Co, and W Absent; Cr High, Cu, Co, and W Absent; Cu Present, Co and W Absent; Neutralization of Solution and Titration of Nickel; Procedure A; Determinations Based on the Ni Value of $\text{AgNO}_3$ ; Procedure B; Determinations Based on Ni Value of the KCN Solution; Cobalt, Tungsten or Both Present: Procedure A, Procedure B; Solutions Required: Ammonium Citrate-Sulphate Solution, etc., Standardization of Solutions.	
NOTES ON SPECIAL PROCEDURES FOR HIGH-CHROMIUM STEELS, STAINLESS AND HEAT-RESISTANT STEELS CONTAINING MUCH OR LITTLE NICKEL; COPPER, COBALT AND TUNGSTEN ABSENT .....	131
Special Solutions Required; Weight of Sample; Procedure.	
THE DIMETHYL GLYOXIME METHOD .....	133
Application of the Method; Weight of Sample; Procedures for Nickel and Chromium-Nickel Steels; Solutions of Dimethylglyoxime Required: Ammoniacal, Alcoholic; Procedure: Weighing as Nickel Dimethyl Glyoxime; Weighing as Nickel Oxide: Titration of the Nickel; Weighing as Metallic Nickel after Electrolytic Separation; Determination of Nickel in High Nickel-High Copper-Chromium Steels: Special "Red Acid" Mixture.	
DETERMINATION OF SMALL PROPORTIONS UNDER 0.05% OF NICKEL OR OF CHROMIUM AND NICKEL .....	136
For Nickel Only; For Cr and Ni.	

## Determination of Chromium

METHODS .....	138
Special Solutions Required: Standard Ferrous Ammonium Sulphate, Standard Oxidant Solutions, Standard 0.1 Normal $\text{KMnO}_4$ ; Standardization of $\text{KMnO}_4$ Solutions with National Bureau of Standards Sodium Oxalate; Weight of Sample.	
METHODS APPLICABLE TO STEELS CONTAINING MORE THAN 0.10% CHROMIUM: PERCHLORIC ACID METHOD OF OXIDATION ...	141
Absence of Tungsten: Solution of Sample and Preparation of Same for Titration of the Chromium; Visual Titration of Cr and V After Oxidation with Perchloric Acid; Special Solution Required: Ferrous Sulphate Phosphoric Acid Mixture; Indicator Solutions: Orthophenanthroline Ferrous Sulphate, Orthophenanthroline Ferrous Perchlorate, Potassium Phosphate, Standard Solutions of $\text{KMnO}_4$ ; Procedure; Presence of Tungsten: Special Solutions Required: Phosphoric-Perchloric Acid Mixture, etc.; Indicator Solution; Procedure.	
PERSULPHATE METHOD OF OXIDATION .....	145
Solution and Preparation of the Sample for Titration of the Chromium; Procedure.	
POTASSIUM PERMANGANATE METHOD OF OXIDATION .....	146
Solution and Preparation of the Sample; Visual Titration of the Cr and V: Procedure for Low and Medium Chromium and Alloy Steels;	



Alternate Procedure for High-Chromium (Stainless and Heat-Resistant) Alloy Steels; Potentiometric Titration of Chromium; Absence of V and W; Titration with the Larrabee Apparatus; Determination of Chromium Using the Larrabee Potentiometric Apparatus.

## METHODS APPLICABLE TO CARBON STEELS AND OTHER STEELS CONTAINING CHROMIUM UNDER 0.10% ..... 150

Procedure Following an Ether Separation of Iron and Mo: Chromium and Nickel to be Determined; To Determine Nickel after Titrating for Cr; Cr, V, and Ni can be determined, etc.; Procedure Using the Bicarbonate Separation; Method Without Separating Iron, Cr and V: Special Mixture Required, Standard  $\text{KMnO}_4$  Solution; Procedure.

## TITRATION OF CHROMIUM BY THE ARSENITE-OSMIC ACID METHOD 152

Arsenite Reduction with Osmic Acid as Catalyst: Procedure; Solutions Required; Blank Due to Indicator; Standardization of Arsenite.

### Determination of Vanadium

## METHODS AVAILABLE ..... 155

## FERROUS SULPHATE-PERSULPHATE-PERMANGANATE METHOD ..... 155

Weight of Sample; Acid Mixture; Procedure: Vanadium and Chromium-Vanadium Steels, Carbon Steels Containing Little V, High-Chromium Steels.

## PERCHLORIC ACID-DIBASIC POTASSIUM PHOSPHATE METHOD .... 157

Method Eliminating Chromium as Chromyl Chloride: Special Solutions Required: Standard  $\text{KMnO}_4$ , Ferrous Ammonium Sulphate Solution, Ammonium Persulphate; Weight of Sample; Procedure: Solution of Sample, Volatilization of Cr by Additions of NaCl, Volatilization of Cr by Additions of HCl, Comparison of Titrating Solutions and Check for Cr, Titration of Vanadium.

## PERCHLORIC ACID-LEAD CHROMATE-POTASSIUM PHOSPHATE METHOD ..... 160

Principle and Application; Procedure: Solution of Sample and Separation of Cr, Removal of  $\text{HClO}_4$ , Reduction and Titration of V; Reagents and Solutions Required: Perchloric Acid, 55%, Ferrous Sulphate-Phosphoric Acid Mixture, Potassium Phosphate Solution, Indicator Solutions; Preparation of Orthophenanthroline Ferrous Sulphate, etc.: Materials, Procedure; Preparation of Orthophenanthroline Ferrous Perchlorate; Preparation of Lead and Silver Perchlorate (0.5 M Solutions).

## NITRIC ACID POTENTIOMETRIC TITRATION METHOD ..... 163

Special Solutions Required: Standard Potassium Dichromate Solution, Ferrous Ammonium Sulphate Solution; Procedure.

## ELECTROLYTIC-SULPHUR DIOXIDE-PERMANGANATE METHOD ..... 164

Principles and Application; Procedure: Solution of the Sample and Separation with Bicarbonate, Electrolytic Separation of V, Reduction and Titration of V.

## COLOR METHOD ..... 166

Special Solutions Required:  $\text{H}_2\text{O}_2$  Solution, Ammonium Vanadate Solution; Procedure: Solution of Sample in Absence of W; Preparation of Standards; Treatment of Sample in Presence of W.

<b>Determination of Molybdenum</b>		<i>Page</i>
<b>METHODS AVAILABLE</b> .....		168
<b>METHODS SEPARATING THE MOLYBDENUM AS SULPHIDE</b> .....		168
Weight of Sample; Procedure: Solution of Sample, Tungsten Absent, Tungsten Present; Precipitation of Mo as Sulphide.		
<b>TREATMENT OF SULPHIDE</b> .....		169
Absence of As, V and Sn; Ignition of $\text{MoS}_3$ to $\text{MoO}_3$ : Weighing Mo as $\text{MoO}_3$ , Precipitation and Weighing as $\text{PbMoO}_4$ ; Presence of As, V, and Sn: Gravimetric Method, Volumetric Method, Separation and Determination of Mo by Alpha-benzoinoxime Method; Special Solutions Required; Procedure.		
<b>COLORIMETRIC METHODS</b> .....		172
The "Photometer"; Extracting Mo with Butyl Acetate: Method Using the "Photometer": Special Solutions Required: Potassium Thiocyanate, Stannous Chloride, Saturated Butyl Acetate; Procedure; Following Volatilization of the Cr and Separation of Mo as Butyl Acetate: Special Solutions and Reagents Required: Sodium Thiocyanate, Stannous Chloride-Tartaric Acid; Procedure for Steels up to .65% Mo: Solution of Sample, Elimination of Cr, Separation of Mo; Determination of Mo with Lange Colorimeter: For Steels Containing .65% to 1.0% Mo, 1-2% Mo, 2-6% Mo.		
<b>METHOD ESTIMATING THE MOLYBDENUM VISUALLY</b> .....		176
Special Solutions Required: Sodium Thiocyanate, Stannous Chloride, Butyl Acetate, Standard Mo Solution; Procedure: Weight of Sample; Solution of Sample.		
<b>COLOR METHOD WITHOUT EXTRACTING MOLYBDENUM</b> .....		178
Solutions Required: Sulphuric-Hydrochloric Acid Mixture, Perchloric Acid, Sodium Thiocyanate (Sulphocyanate) Solution, Stannous Chloride Solution, Chromium-Potassium Sulphate Solution, Ferric Sulphate— $\text{HCl-H}_2\text{SO}_4$ Mixture, Ferromolybdenum Standard Stock Solution, Standard Solutions: Low Standard, High Standard; Weight of Sample; Solution of Sample; Estimation of Mo: Absence of Tungsten and Copper: Cr under 5% or Absent; Cr and Cr-Ni Steels (Stainless and Heat-resistant): Special Solution Required: Chromium-Potassium Sulphate Solution; Presence of Tungsten; Tungsten Steel.		
<b>Determination of Titanium</b>		
<b>METHODS AVAILABLE</b> .....		182
Gravimetric, Volumetric, Colorimetric.		
<b>COLORIMETRIC METHODS</b> .....		183
Apparatus; Special Solutions Required: Standard Ti Solutions, Standard Ti Sulphate Solution, Standard Ti Perchlorate Solution.		
<b>RAPID DETERMINATION OF TITANIUM AND TITANIA BY COLOR IN CARBON STEELS; VANADIUM ABSENT</b> .....		185
Special Solution Required: Perchloric Acid (55%); Procedure for Ti over .02%; Procedure for Ti under .02%; Solution of Sample and Separation of $\text{TiO}_2$ ; Separation of Ti.		
<b>PERCHLORIC ACID-LEAD CHROMATE-HYDROGEN PEROXIDE METHOD FOR CHROMIUM STEELS: COLOR METHOD</b> .....		187
Visual Comparison: Special Solutions Required: Lead Perchlorate Solution, Blank Solutions; Procedure; Comparison by Lange Colorimeter: Solutions Required; Weight of Sample; Procedure.		

	<i>Page</i>
<b>METHODS EMPLOYING PRELIMINARY SEPARATION WITH CUPFERRON</b>	189
Weight of Sample; Special Solution Required: Cupferron (6%); Procedure: Solution of Sample and Treatment of Residue, Separation with Cupferron; Determination of Ti by Color: In Perchloric Acid Solution, In sulphuric Acid Solution.	
<b>GRAVIMETRIC AND VOLUMETRIC METHODS</b>	192
Cupferron Ammonium Sulphide Method: Weight of Sample; Procedure; Umpire Method for Titanium in Steels Using the Thio-sulphate-Phenylhydrazine Method of Separation: Principles of the Method; Procedure.	
<b>Determination of Aluminum</b>	
<b>METHODS AVAILABLE</b>	197
Total Alumina, Metallic Aluminum, and $Al_2O_3$ in Steel.	
<b>METHOD FOR DETERMINATION OF TOTAL ALUMINUM IN STEEL</b>	198
Method Using the Bicarbonate Separation: Application of the Method; Weight of Sample; Special Solutions: Cupferron Solutions, Blanks; Procedure: Solution of Sample and Separation with Bicarbonate: NaOH Separation, Separation of Cu, etc. as Sulphides; Separation with Cupferron; Separation of Al with Ammonia; Determination of Al as Phosphate.	
<b>METHOD USING ETHER SEPARATION</b>	201
Solution of Sample; Separation of $Fe^{+++}$ with Ether; Oxidation of Cr and Separation with Ammonia.	
<b>THE PHOSPHATE METHOD</b>	202
Weight of Sample; Blank Test; Procedure: Solution of Sample; Presence of Tungsten, Absence of Tungsten; First Separation of Al, etc. as Phosphate; Separation of Cr, Ti, etc.; Final Precipitation as Phosphate.	
<b>METHODS FOR THE DETERMINATION OF METALLIC ALUMINUM AND <math>Al_2O_3</math> IN STEEL</b>	204
Procedures for Determination of Insoluble Alumina: Weight of Sample; Solution of Sample; Analysis of Residue; Electrolysis over Mercury Cathode; Precipitation of Al as Phosphate; Procedures for Determination of Metallic or Soluble Alumina: Bicarbonate Separation followed by Electrolysis over Mercury Cathode; Procedure.	
<b>STANDARD PROCEDURE FOR DETERMINATION OF METALLIC OR SOLUBLE ALUMINUM</b>	207
Final Precipitation with 8-Hydroxyquinoline and Titration of Aluminum Quinolate: Weight of Sample, Solutions Required, Blank; Procedure: Solution of Sample; Separation by Hydrolysis, with $SO_2$ and Ammonia; Alternate Separation with Sodium Bicarbonate; Separation with NaOH: Procedure Following $SO_2$ -Ammonia Separation, Procedure Following Bicarbonate Separation; Separation by Electrolysis over Mercury Cathode; Precipitation of Aluminum with 8-Hydroxyquinoline: Titration of Aluminum Quinolate. Calculation, Blank.	
<b>PROCEDURES FOR ALUMINUM AND ALUMINA IN HIGH-CHROMIUM STEELS INCLUDING STAINLESS AND HEAT RESISTANT STEELS</b>	212
Lead Chromate Separation Followed by Titration of Aluminum as the Quinolate; Solution of Sample and Separation of $Al_2O_3$ . Oxidation and Separation of Chromium, Removal of Excess Lead and Sulphide; Determination of Aluminum; Determination of Alumina; Solutions Required.	

	<i>Page</i>
DETERMINATION OF TOTAL ALUMINUM IN HIGH-SILICON STEELS ..	214
Solution of Sample; Initial Separation with Phosphate; Separation by Hydrolysis Over a Mercury Cathode; Precipitation and Determination of Aluminum as Phosphate.	
<b>Determination of Arsenic</b>	
OCCURRENCE OF ARSENIC IN STEEL.....	217
Methods Available; Blanks.	
METHODS FOR SOLUTION OF SAMPLE AND SEPARATION OF THE ARSENIC.....	218
Procedure for Dissolving Sample in $\text{HNO}_3$ Followed by Reduction and Distillation of the $\text{AsCl}_3$ : Solution of Sample, Separation of Arsenic; Procedure Dissolving in a Mixture of $\text{HCl}$ and $\text{KClO}_3$ : Solution of Sample.	
METHODS FOR DETERMINATION OF ARSENIC.....	219
Gravimetric Method Weighing as $\text{As}_2\text{S}_3$ ; Volumetric Method Titrating with $\text{KBr}$ ; Principles of the Method, Special Solution Required, Procedure.	
<b>Determination of Tin</b>	
OCCURRENCE OF TIN AND METHODS AVAILABLE .....	221
METHODS OF DETERMINATION.....	222
Special Solution Required: Standard Iodine or Potassium Iodate; Distillation: Volumetric Method: Application of the Method; Weight of Sample; Procedure: Solution of Sample and Separation of Tin, Reduction of $\text{SnCl}_4$ and Titration of $\text{SnCl}_2$ .	
UMPIRE METHOD.....	223
Weight of Sample; Solution of Sample: Procedure for Irons, Plain-Carbon Steels, and Alloy Steels Decomposable by Nitric Acid: Treatment when Tungsten is Absent, Treatment when Tungsten is Present; Procedure for Alloy Steels not Decomposable by Nitric Acid: Treatment in Absence of Tungsten or other Insoluble Matter, Treatment in Presence of Tungsten or other Insoluble Matter; Precipitation and Separation of Tin with $\text{H}_2\text{S}$ and Ammonia; Reduction and Titration of Tin.	
RAPID CONTROL METHOD FOR TIN.....	226
Solution of Sample in $\text{HCl}$ Followed by Direct Titration of Tin: Special Solutions Required; Apparatus; Procedure.	
<b>Determination of Cobalt</b>	
ZINC OXIDE-ALPHA NITROSO BETA NAPHTHOL METHOD.....	229
Special Reagents Required; Procedure: Solution of Sample and Separation with $\text{ZnO}$ , Precipitation of Cobalt.	
VOLUMETRIC METHOD.....	231
Direct Titration of $\text{Co}$ and $\text{Ni}$ with Potassium Cyanide; Special Solutions Required; Procedure: Solutions Required.	
DETERMINATION OF SMALL PERCENTAGES OF COBALT AS IN PLAIN-CARBON STEELS.....	233
Cobalt under 0.10 per cent: Procedure.	

Determination of Tungsten		Page
USE OF TUNGSTEN AND METHODS FOR ITS DETERMINATION . . . .		234
Weight of Sample, Method for Checking Silicon Results: Special "Phosphodant" Solution Required; Procedure.		
THE HYDROCHLORIC ACID-NITRIC ACID-CINCHONINE-SODIUM CARBONATE FUSION METHOD FOR SILICON AND TUNGSTEN OR TUNGSTEN ALONE . . . . .		235
Special Solutions of Cinchonine Required; Procedure for All Steels Except High-Speed Steels: Absence of Much Vanadium, Silicon Desired; Presence of Much Vanadium, Silicon not Desired.		
PERCHLORIC ACID-CINCHONINE-SODIUM HYDROXIDE SOLUTION METHOD . . . . .		237
Special Cinchonine Solutions Required; Procedure.		
THE ALPHA-BENZOINOXIME METHOD FOR LOW PERCENTAGES OF TUNGSTEN . . . . .		238
Special Solutions Required; Procedure.		
VOLUMETRIC METHOD FOR LOW TUNGSTEN . . . . .		239
PROCEDURE FOR DETERMINATION OF TUNGSTEN IN HIGH-SPEED STEELS . . . . .		239
Determination of Uranium		
OCCURRENCE AND METHODS AVAILABLE . . . . .		241
PROCEDURE DISSOLVING THE SAMPLE IN SULPHURIC OR HYDROCHLORIC ACID WITH FINAL PRECIPITATION WITH CUPFERRON . . . . .		241
Solution in Sulphuric Acid: Treatment of Residue in Absence of W, Treatment of Residue in Presence of W; Separation of Uranium with Ammonia Following Solution in $H_2SO_4$ : Solution in HCl, Separation of Iron with Ether; Separation with Cupferron.		
PROCEDURE DISSOLVING THE SAMPLE IN HYDROCHLORIC ACID WITH FINAL PRECIPITATION WITH AMMONIA . . . . .		243
Solution of Sample and Separation of W; Separation with Ether; Separation of Manganese; Separation with Ammonia; Separation with Ammonia and Sodium Carbonate; Final Precipitation of Uranium with Ammonia.		
Determination of Zirconium		
METHODS AVAILABLE . . . . .		245
Precipitation with Diammonium Phosphate; Precipitation with Cupferron, etc.; Precipitation with Phenylarsonic Acid.		
METHODS DEPENDENT UPON SEPARATING AND WEIGHING ZIRCONIUM AS PHOSPHATE . . . . .		246
Direct Perchloric Acid-Phosphate Method for Zr in Plain-Carbon and Stainless Steels, Absence of Cb, Ta, W and Sn; Phosphate-Hydrogen Peroxide Method, Absence of Cb, Ta and Sn; Direct Phosphate Method in Reduced Solution for Zr in Carbon and Low-Alloy Steels in Absence of Cb, Ta and Sn; Complete Phosphate Method Modified for Application to all Steels Except High-Chromium: Solution of Sample in Absence of W, Solution of Sample in Presence of W, Reduction of Iron and Separation of Cu, etc., Precipitation with Phosphate.		

# STANDARD PROCEDURES BASED UPON SEPARATION OF ZIRCONIUM WITH CUPFERRON ..... 251

Cupferron Phosphate Method in Absence of Cb, Ta and Sn; Cupferron Solution Required; Weight of Sample; Procedure: Solution of Sample and Separation with Cupferron, Precipitation as Phosphate.

## METHODS DEPENDING ON SEPARATION OF ZIRCONIUM WITH PHENYL-ARSONIC ACID AND WEIGHING AS ZIRCONIUM OXIDE..... 252

Special Solution Required; Procedure Involving a Preliminary Separation with Ether; Solution of Sample: Presence of Tungsten, Absence of Tungsten; Precipitation of Zirconium; Procedure Involving a Double Precipitation with Phenylarsonic Acid Without a Previous Separation: Solution of Sample, Precipitation of Zirconium; Procedure Using Double Precipitation with Phenylarsonic Acid for Stainless and other High-Alloy Steels Containing No Tungsten.

## PROCEDURE ADAPTING THE PHENYLARSONIC METHOD TO THE DETERMINATION OF SILICON AND ZIRCONIUM, TUNGSTEN AND COLUMBIUM..... 255

Special Reagents Required; Procedure: Columbium and Tungsten Absent: Solution of Sample, Separation and Determination of Silicon, First Precipitation of Zirconium, Recovery of Zr from Si Residue, Treatment to Determine Total Zr; Columbium Present, Tungsten Absent: First Precipitation of Cb, Fusion of Residues, Separation and Determination of Cb, Recovery and Determination of Cb, Recovery and Determination of Zr; Columbium and Tungsten Present: Recovery of Zr, Cb and Tungsten, First Precipitation of Zr, Separation and Recovery of Zr from the Residues and Estimation of Tungsten in the Absence of Columbium, Recovery and Determination of Zr, Separation and Determination of Cb and W, Estimation of Tungsten.

### Determination of Columbium and Tantalum

## METHODS AVAILABLE..... 260

## PROCEDURE FOR DETERMINATION OF SILICON AND COLUMBIUM IN STAINLESS AND ALLOY STEELS CONTAINING NO TUNGSTEN OR TANTALUM: GRAVIMETRIC METHOD..... 261

Application and Accuracy of the Method; Procedure: Solution of Sample and Separation of Si, Determination of Si and Recovery of Cb, Recovery and Determination of Cb.

## PROCEDURE FOR DETERMINATION OF COLUMBIUM AND TANTALUM IN STAINLESS AND HEAT-RESISTANT STEELS: ABSENCE OF TUNGSTEN OR MUCH TITANIUM: GRAVIMETRIC-VOLUMETRIC METHOD..... 262

Applications and Accuracy of the Method; Special Solutions Required; Special Apparatus; Jones Reductor; Procedure: Solution of Sample and Separation of Cb and Ta, Determination of Cb.

## PROCEDURE FOR DETERMINATION OF COLUMBIUM (SILICON AND TANTALUM) IN STAINLESS AND HEAT-RESISTANT STEELS: PRESENCE OR ABSENCE OF SELENIUM, TITANIUM, AND ZIRCONIUM..... 266

Procedure: Solution of Sample and Separation of Si; Determination of Si; Separation and Recovery of Cb.

	<i>Page</i>
PROCEDURE FOR DETERMINATION OF TANTALUM (AND COLUMBIUM)	268
Solution and Separation of Iron, etc.; Separation and Determination of Tantalum.	
METHOD FOR COLUMBIUM AND TANTALUM, TITANIUM AND ZIRCONIUM.....	269
Special Solutions and Apparatus Required; Weight of Sample; Procedure: Solution of Sample and Separation of Cb, Ta, Ti and Zr: Absence of Tungsten, Presence of Tungsten; Separation of the Elements in the Mixed Oxides; Determination of Ti; Determination of Cb.	
<b>Determination of Selenium</b>	
METHODS AVAILABLE.....	273
STANDARD VOLUMETRIC METHOD FOR STAINLESS STEELS, SELENIUM BEING SEPARATED WITH SULPHUR DIOXIDE AND TITRATED WITH POTASSIUM IODIDE AND SODIUM THIOSULPHATE ....	273
Special Solutions and Reagents Required: Special Reagent, Starch Solution, Standard Sodium Thiosulphate Solution, Standard Iodine Solution, Hydrochloric-Sulphurous Acid Solution; Procedure: Solution of Sample and Separation of Se; Solution and Titration of Se.	
VOLUMETRIC METHODS.....	274
Hydrogen Chloride Bromide Iodide Method: Special Apparatus and Reagents Required; Procedure; Perchloric-Nitric Acid Iodide Method for Stainless Steels: Method of Marvin and Schumb; Procedure.	
GRAVIMETRIC METHODS.....	277
Iodine Solution $\text{HClO}_4\text{-SO}_2$ Method: Presence of Tellurium; Precipitation of Se by the $\text{HCl-SO}_2$ Method in Absence of Tellurium; Precipitation of Se by the Iodine-Citric Acid Hydroxylamine Hydrochloride Method in Presence of Tellurium.	
METHODS INVOLVING SOLUTION IN ACIDS, PRECIPITATION WITH SULPHUR DIOXIDE AND VOLATILIZATION OF SELENIUM....	279
Solution of Sample and Separation of Se; Purification and Determination of Se; Copper Chloride-Perchloric Acid Method: Special Solutions Required: Zinc Oxide Nitric Acid Reagent, Copper-Potassium Chloride Solution; Procedure.	
<b>Determination of Boron</b>	
OCCURRENCE OF BORON.....	282
METHODS AVAILABLE.....	282
Special Solutions Required: Phenolphthalein Indicator Solution, Mannite, Standard $\text{NaOH}$ Solution.	
PROCEDURE USING ELECTROLYSIS OVER MERCURY CATHODE AND CALCIUM CARBONATE.....	283
Solution of Sample and Separation by Electrolysis; Titration of $\text{H}_3\text{BO}_3$ in Absence of Al, etc.; Separation with $\text{CaCO}_3$ and Titration of $\text{H}_3\text{BO}_3$ .	
METHOD BASED ON CALCIUM CARBONATE SEPARATION.....	284
<b>Determination of Beryllium</b>	
OUTLINE OF PROCEDURE.....	286

Determination of Nitrogen		Page
EFFECTS OF NITROGEN AND METHODS AVAILABLE.....		287
STANDARD SOLUTION AND DISTILLATION METHOD: DIGESTION IN SULPHURIC AND ORTHOPHOSPHORIC ACIDS FOLLOWED BY INDIRECT TITRATION WITH POTASSIUM IODIDE, POTASSIUM IODATE AND SODIUM THIOSULPHATE.....		288
DETERMINATION OF NITROGEN IN PIG IRON AND STEEL.....		288
Apparatus; Special Reagents and Solutions Required; Blank; Procedure: Solution and Digestion of Sample; Daily Titration Blank; Method for Standardizing Iodine and Sodium Thiosulphate Solutions; Calculation.		
MODIFIED METHOD EMPLOYING ACID-ALKALI TITRATION WITH METHYL RED AS INDICATOR.....		295
Special Solutions Required; Procedure: Weight of Sample; Reagent Blank; Daily Titration Blank; Calculation of Results.		
METHODS FOR DETERMINATION OF NITROGEN IN STAINLESS STEEL		298
Solution of Sample in HCl: with Digestion of Insoluble Residue in $\text{H}_2\text{SO}_4$ , Absorption of $\text{NH}_3$ in HCl and Titration of Excess with NaOH; Special Reagents Required; Solution of Sample.		
Determination of Antimony, Copper and Molybdenum		
STANDARD PROCEDURE.....		300
Solution of Sample: Steels and Irons Soluble in Nitric Acid; Steels and Irons Not Soluble in Nitric Acid; Precipitation with $\text{H}_2\text{S}$ ; Ammonia Separation of Cu and Mo; Separation of Arsenic; Reprecipitation and Determination of Antimony.		
Determination of Zinc		
OCCURRENCE AND METHODS AVAILABLE.....		303
PROCEDURE MAKING THE INITIAL SEPARATION AS SULPHIDE....		303
Solution of Sample; Precipitation of Zinc; Separation of Zinc as Sulphide; Final Separation of Zinc.		
PROCEDURE SEPARATING IRON AND ZINC WITH AMMONIA.....		305
Separation of Iron; Separation and Determination of Zinc.		
PROCEDURE SEPARATING IRON WITH ETHER.....		305
Separation of Iron with Ammonia.		

### Determination of Cerium

OUTLINE OF METHOD FOR DETERMINATION OF CERIUM.....	307
--	-----

### Appendix I: Determination of Sulphur or Carbon and Sulphur by Combustion in Oxygen

PROCEDURE OF HALE AND MUEHLBURG.....	322
Apparatus and Reagents: Oxygen Supply, Reducing Valves, Oxygen Purifying Train, Pressure Regulator and Auxiliary Oxygen Supply, Electric Furnace, Rheostat and Pyrometer, Combustion Tube, Combustion Boat, Sulphur Absorber, $\text{CO}_2$ Absorber, Flow Indicator.	



	<i>Page</i>
REAGENTS FOR ABSORPTION AND TITRATION OF SULPHUR.....	317
H <sub>2</sub> O <sub>2</sub> Solution, Standard H <sub>2</sub> SO <sub>4</sub> , Methyl Red Indicator Solution, Standard NaOH.	
SOLUTIONS FOR DETERMINING CARBON VOLUMETRICALLY.....	319
CO <sub>2</sub> -Free Water; Barium Hydroxide Solution, Standard HCl Solution, Indicator Solution; Testing and Care of Combustion Train; Correct Temperatures for Different Steels; Procedure: Case I, Case II: Pro- cedure; Case III.	
PROCEDURE OF WOODWARD AND WALTHORNE (YOUNGSTOWN WORKS, CARNEGIE-ILLINOIS STEEL CORPORATION) FOR DETERMINATION OF SULPHUR IN CARBON AND LOW-ALLOY STEELS AND NON-METALLIC SUBSTANCES.....	326
Application and Principles of the Method: For all materials; For metallic materials; For non-metallic substances; Method of Standard- izing NaOH; Procedure in Titrating; Absorption Equipment; List of Equipment; Solutions Required; Procedure: Testing the Equip- ment and Technique with Standard Sodium Sulphate Solution; Variations in the Procedure for Sulphur in Steels: The Sample, Weight of Sample.	
PROCEDURE AS USED BY L. P. CHASE, SOUTH WORKS, CARNEGIE- ILLINOIS STEEL CORPORATION.....	334
Apparatus; Special Solutions Required; Procedure.	
<b>Appendix II: Discussion of Methods for Oxygen, or Oxygen, Hydrogen and Nitrogen in Steel</b>	
VACUUM FUSION METHODS.....	337
HYDROGEN REDUCTION METHOD.....	338
METHODS BASED ON DETERMINATION OF OXIDES OR OXIDE INCLU- SIONS HELD IN STEEL IN THE SOLID STATE.....	339
Iodine Method, Chlorine Method, Electrolytic Solution Method, Mercuric Chloride Solution Method.	
ACID SOLUTION METHODS.....	340
Nitric Acid or Dickenson Method, Sulphuric Acid Method, Hydro- chloric and Perchloric Acid Methods, Microscopic Method.	
<b>Appendix III: Preparation, pH Ranges, and Color Changes of Various Organic Chemical Indicators</b>	
NORMALITY AND pH VALUES.....	342
METHODS FOR DETERMINING pH OF SOLUTIONS.....	343
NOTES ON INDICATORS.....	348
<b>Appendix IV: Table of Atomic Weights, Atomic Numbers, and Other Physical Constants of the Chemical Elements</b>	
	351

# Sampling

## Introductory Remarks

The self-evident fact that the analysis can be no more representative of the material than the sample is sufficient to emphasize the importance of correct methods for carrying out the work of sampling. This statement applies to any material, but the high cost of many of the alloy steels lends additional importance to the matter.

Not only is steel sampled during the processes and operations of its manufacture, but also after it has been worked into the various products of the steel plants. These materials may be sampled at various stages in their processing and fabrication, and the methods of sampling employed are necessarily varied to meet different conditions and must be adjusted to different kinds and grades of steel as well as to the different physical forms in which the materials are presented for sampling. So far as possible, these conditions have been classified and are discussed along with methods applicable to each class, as follows:

## Preliminary Tests

### Sampling

**Tests for Drilling.**—In the crucible or the electric process employing the induction furnace, sampling the steel before it is poured is difficult and is seldom attempted. With other furnaces, however, testing is carried on during the making of a heat and has for its object the control of the composition and properties of the finished product. Such tests and analyses must usually be made very quickly, and with this object in mind the methods of sampling will be varied according to the object sought. By the older procedure, the test is taken in a slagged spoon, killed with aluminum if desirable, cast in a suitable mold, usually with a capacity of about 2 pounds, and drilled to obtain the sample for analysis. A mold of suitable design and size, which may be modified by making it of the split mold type, is shown in the drawing of Fig. 1. Our investigations have proved that tests cast in the melters' fracture test mold are generally unsatisfactory, the test being difficult to drill and prone to contain defects which make the results of the analysis erratic and unreliable. A spoon of a size to fill the mold recommended is shown in the drawing of Fig. 2.

### Rapid Methods for Preliminary Tests

To assure a sound, uniform test best for drilling for chemical analysis, aluminum must be added for most heats, and is generally added

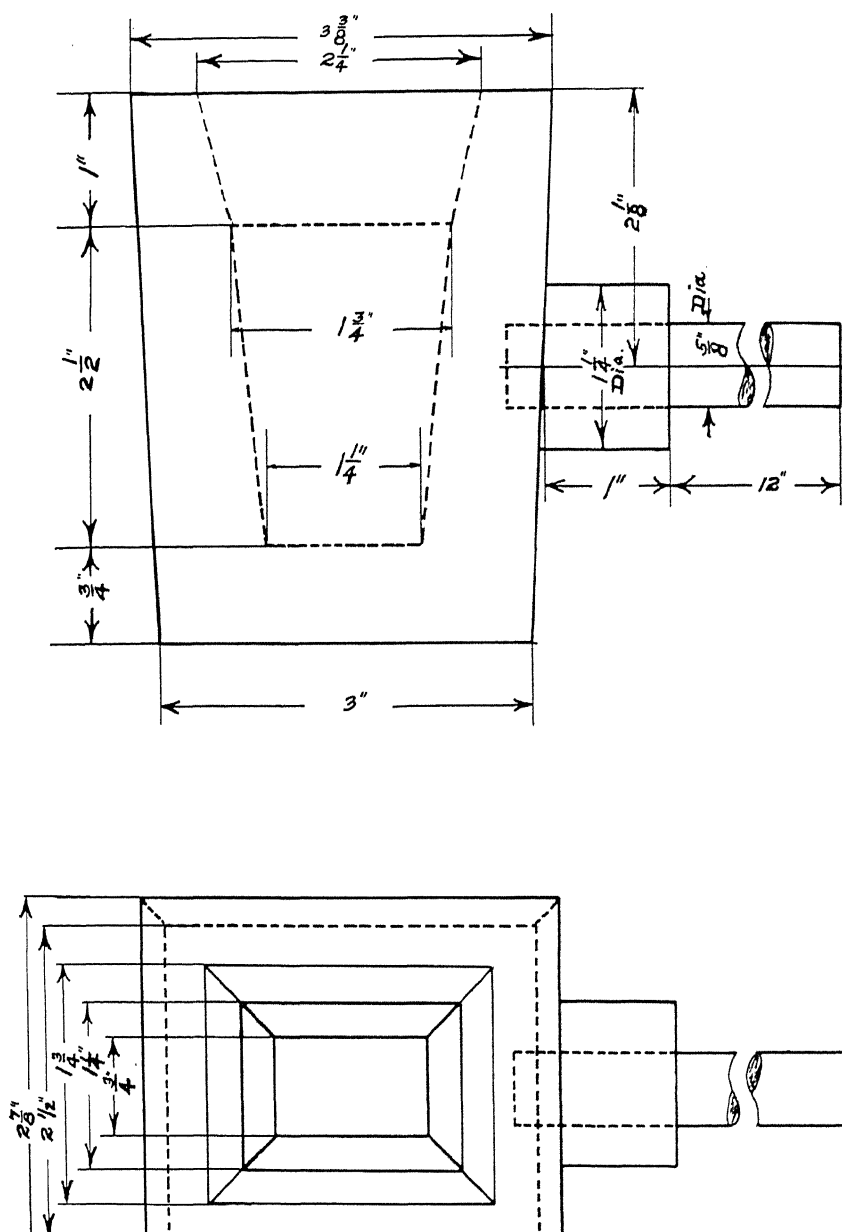


FIGURE 1. Working drawings for preliminary test mold

to all preliminary tests that are not to be used for the determination of Al or  $\text{Al}_2\text{O}_3$ . The aluminum used is in the form of wire, which is purer and much more satisfactory than aluminum in the form of shot is likely to be. The test is drilled with a  $\frac{3}{4}$ -inch flat, beaded, high-speed drill at a point over the central axis and  $1\frac{1}{4}$  inches from the bottom, the first drillings being discarded and the sample obtained by drilling to the center or until the point of the drill just appears on the opposite side.

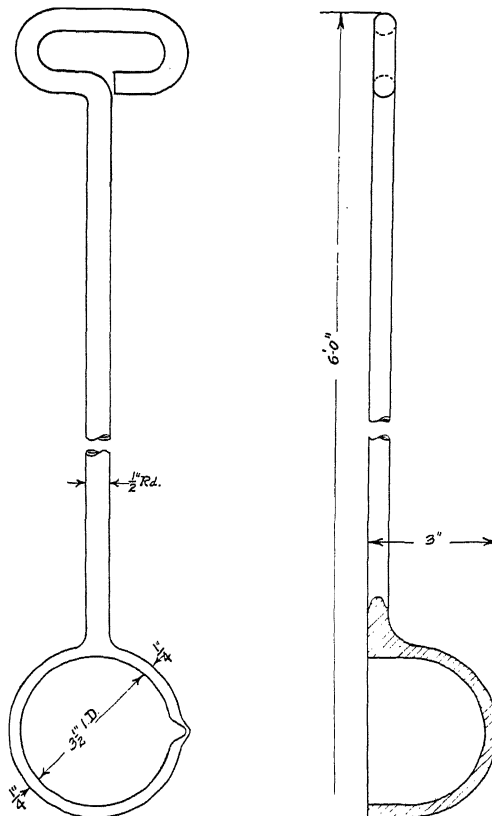


FIGURE 2. Working drawings of spoon used for taking preliminary tests.

At best, the method described above is slow, and frequently the metal to be tested cannot be drilled readily, necessitating the use of some other method, such as crushing, for preparing the sample. To meet these conditions, either the patented methods (see U. S. Patents, Nos. 1933425 and 1977737), commonly known as the "thimble test"

and the "subslag test" are used; or the metal is cast in a special mold designed to give a very thin section projecting like a fin from a lower section of the test so that it may be broken off and crushed to small sizes. In the "thimble test," the liquid metal sample is obtained with a spoon in the usual way, but instead of pouring into a mold, a thin thimble-shaped test piece is obtained by quickly immersing the nose of the sampling tool into the spoon and immediately plunging it into cold water. In some cases it is desirable to kill the metal in the spoon, by raking off the slag and plunging a piece of aluminum wire into the metal before immersing the sampling tool. This method gives a test piece free of scale, and since the metal clinging to the sampling tool is solidified almost instantly, it gives a test free of segregation. With certain alloy steels and plain-carbon steels containing more than 0.35 per cent carbon, the test piece is so brittle it may be crushed to very small pieces in a steel mortar with a few blows of the pestle, and any slag or scale adhering is quickly separated by sieving. If the sample is taken with care, it is free of both oxide and scale. Metal containing little carbon gives a softer test piece which can be broken with the pestle or cut with shears into small pieces. This method can also be used to sample steel made in crucibles or induction furnaces. The only objection cited against the method is that, on some steels, it gives particles which do not dissolve in acids as rapidly as millings or drillings, hence is not as desirable for the determination of sulphur by the evolution method.

### Sampling under Specifications

#### Size of Samples

In the preceding methods applied to control the processes of manufacture, the sample is used for a limited number of determinations and is of value for immediate use only. Hence, its retention may be required only for a brief period. In the methods that follow, however, a sample sufficient to supply material for a great number of determinations may be necessary, and either the sampling or the analysis may be questioned months after the analysis has been reported. Therefore, it is desirable to take precautions to see that the sample prepared for analysis is ample to provide at least twice the amount required for all the determinations to be made, and that any portion remaining be retained in a suitable container for 6 months to a year. In lieu of the chips or cuttings actually used for analysis, the complete test piece from which they were taken may be preserved, and may be preferable to the cuttings in many instances. The weight of cuttings required for analysis will vary from 10 g to 50 g, according to the number and kind of determinations to be made, the elements to be determined, and the percentages of the elements present.

## Marking for Identification

Identification of samples is extremely important, and all containers of cuttings are labeled, giving the date and all other information necessary for complete identification, such as heat number, slab number, serial number, order number, name of works or customer, etc. Test ingots and test pieces are stamped or indelibly marked with at least one number which is the same as that appearing on the container for the cuttings. When the section is too small to permit stamping, suitable labels are attached with fine wire.

## The Ladle Test

### Sampling

Irrespective of the nature of the requirements that are to be met by the finished product, the ladle test analysis forms the basis of specifications to which all steels are and must be made. Also, numerous and exhaustive investigations have shown that, provided the work of sampling is properly done, the ladle test analysis is more nearly representative of the average composition of a melt than any analysis from samples taken subsequent to casting. The importance of care in making this test, therefore, cannot be too strongly emphasized, and on this account the essential equipment and the procedure for sampling a melt properly are given below in detail.

### Number of Tests

At least one ladle test is taken to represent each melt or heat; and, when required, 2 to 5 tests are taken, these duplicate tests being applied particularly to large tonnages, such as open-hearth heats. If but one test is required, it is taken when the melt is half teemed. The object in taking more than one test is to determine the uniformity of the ladle of steel with respect to some element or elements, and the tests are distributed according to the condition that may be the cause of the variation. For example, when 2 tests are required, the second may be taken during the teeming of the last third of the heat or the next to the last ingot, if slag reaction is feared; or the first test may be taken when one-third has been teemed, and the second when two-thirds of the heat has been teemed, if it is desired merely to check the ladle mixing conditions and make sure the heat is uniform. This extra sampling is justified in the making of highly alloyed steels and in the production of special carbon steels requiring adjustments and modifications of the metallurgical practices. Some standard specifications require that more than one ladle test be taken and prescribe not only the distribution of the tests, but also, how the results of the analysis of each test are to be used to determine whether or not the heat is acceptable.

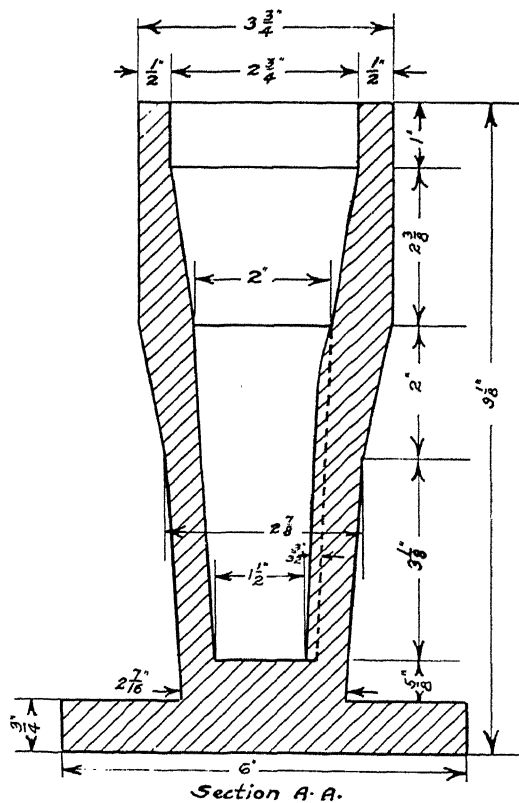
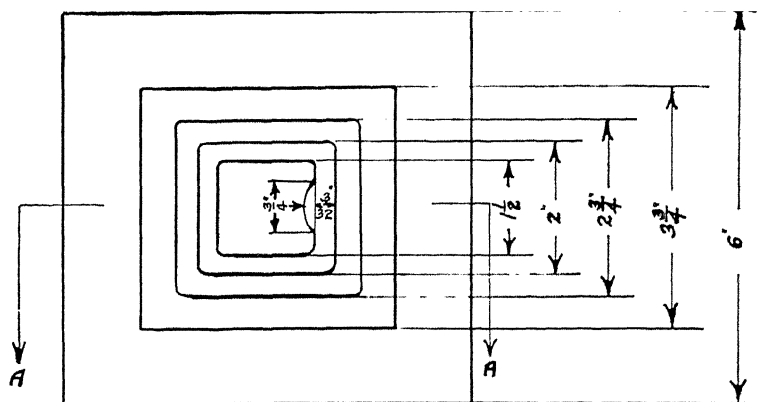


FIGURE 3. Drawings showing the form and dimensions of the standard mold for taking the ladle test.

## Procedure

To take the test, the stream of metal from the nozzle of the ladle is momentarily halted by lowering the stopper; a spoon containing aluminum, if required, as explained in the next paragraph, is held under the nozzle of the ladle, and a sufficient amount of metal to fill the spoon is collected by raising the stopper slightly. The metal is then quickly poured into a mold of a type shown in Fig. 3, being completely killed with additional aluminum as may be desired or required.

## Use of Aluminum to Kill the Test

Aluminum is used when required to kill the steel for the test. The proportion of aluminum requires attention; no more should be used than is necessary to kill the steel, and the actual amount varies with the size of spoon and the kind of steel. As a rule, test pieces of all carbon steels and alloy steels in which the alloying elements themselves do not act as deoxidizers should be killed with aluminum, except those tests that are to be used for the determination of aluminum or alumina. Failure to kill the test properly results in the loss of one to two points of carbon and one to three points of manganese and may give a highly segregated and a very unsound test piece, variable in composition and difficult to drill. When aluminum is used, it is added to the spoon preferably in the form of No. 16 or lighter-gauge wire. The wire is cut in lengths to give the weight desired, coiled about a one-half inch round or square, and placed in the spoon. Wire in this form is preferable to aluminum in the form of pellets, because the latter are often trapped in the "skull" of the spoon, which is the steel that is quickly solidified as it comes in contact with the cold bottom of the spoon. The aluminum thus trapped may fail to act upon the steel that remains liquid and is poured into the mold.

## Mold for the Ladle Test Ingot

Working drawings of the mold in which it is recommended the ladle test sample be cast are shown in Fig. 3. This mold is the result of exhaustive studies made not only by us but by other organizations as well. Reasons for its design and dimensions are briefly stated thus: (1) The investigations referred to have shown that, while several different types of molds give satisfactory results, those giving a portion conforming in section to that of a square ingot are preferable. Hence, standard specifications touching the subject refer to the specimen as the "Ladle Test Ingot." (2) Since a small ingot is subject to piping and segregation like a large ingot, except to a lesser degree, the ingot portion is preferably of the inverted type and topped by a sinkhead large enough to assure that the ingot portion will not contain any pipe under the varying conditions of sampling the many different kinds of steel to be tested. (3) The mold may be of the split type, but such



molds, unless kept in prime condition, give a *test ingot* with fins projecting from diagonally opposite corners, and these fins are objectionable from the standpoint of both safety and convenience in drilling. (4) A one-piece mold must be cast with the inner walls tapering slightly from the bottom to the top to permit the ingot to be removed easily and without delay, and should be provided with a base to support it in an upright position during the pouring. (5) The sectional dimensions of the test ingot must be such that drilling at one point with a drill of moderate size, approximately three-fourths inch, will give sufficient cuttings after a proper discard to provide a sample sufficient in amount for all the determinations to be made, plus a suitable reserve. (6) In the design of Fig. 3, one side of the test ingot is slightly concave to make it self-centering for drilling.

### Marking for Identification

After the test has been poured, it is die-stamped with the heat number for identification, then cooled rapidly by quenching in water, allowed to cool in the air, or cooled slowly in an annealing furnace, the rate of cooling being adapted to the type of steel so as to obtain a test piece that can be drilled most readily, and give drillings in a condition best suited for analysis. The corrosion and heat resisting steels and other unstable austenitic steels require rapid cooling to obtain them in a condition of lowest hardness.

### Drilling

The sample for analysis is obtained by drilling with a three-quarter to one-inch flat beaded drill of a suitable grade of high-speed steel from a point about  $1\frac{3}{4}$  inches from the bottom of the test piece, and over the center of the middle third of the portion of the test below the sinkhead. The drill must be kept properly hardened and sharpened, and the feed of the press must be maintained within certain limits to obtain suitable drillings. If the feed is too fast, the drillings will be too coarse; if too slow, the drill will not bite into the metal, which will work-harden and will become somewhat difficult to drill. The first drillings are discarded until the edges of the drill are cutting into clean metal, after which point the drillings are collected in a suitable metal catch-pan until a sufficient amount has been collected for the analysis desired, usually 30 to 40 g. Drilling is continued until the drill has penetrated to a depth equal to half the thickness of the test piece or entirely through. Extreme care is taken to keep the drillings free of oil, grease, dust, or any other foreign matter.

### Sieving the Cuttings

As a further precaution against contamination of the sample, also to obtain drillings best suited to certain determinations, such as carbon, the drillings are sieved on a nest composed of a No. 10 and a

No. 60 sieve. With most grades of steel the fines passing the latter sieve are discarded, while the cuttings that remain upon both sieves are retained separately, the No. 10 by 60 size for carbon and any other determinations requiring small cuttings for close weighing or rapid solution. Discarding the fines is not always permissible, for in certain high-carbon steels, particularly if the sample has been obtained by milling or by drilling at slow feed, the fines contain carbide constituents of the steel derived from the coarser material. Therefore, this procedure of sieving on a 60-mesh sieve is permissible and desirable where the amount of fine dust in the sample is very small. It should not, however, be used on samples containing any appreciable amount of fine dust, such as is obtained on many milled samples. With these samples, care should be used to weigh an average mixture of the entire sample to avoid error from this segregation of carbides in the fine material.

### Sampling from Blooms and Billets

Billets are sampled occasionally to check the mill practice; also, with certain grades of steel of high quality, blooms and billets are sampled to make sure all parts of a heat will meet the specifications or the requirements of the use to which it is to be applied. This exploration of the heat is made necessary mainly by the natural phenomenon known as segregation, which varies considerably in degree, depending upon the grade and type of steel and other factors. Samples are obtained from billets by milling a complete cross-section, by sawing half or all the way through the section, or from blooms and billets by drilling in a direction parallel to the axis at a point located one-half to two-thirds of the distance from the center to the surface of the cross-section of the bloom or billet measured on the diagonal. This location for drilling gives a sample as nearly representative of the material as can be had by this method of sampling, and this practice is followed except when special investigations are being made, in which case the drillings may be taken from any point or points, according to the object of the investigation. Occasionally, the conditions under which the drilling of blooms and billets must be done are not favorable to the best sampling. For example, pieces of blooms and billets sheared hot are difficult to drill so as to obtain a representative sample on account of the deformation produced by the shear. On the sheared edge, the shear blade produces a displacement of metal known as the "drag," which makes it difficult to locate a point midway between the center and a side or edge. Therefore, if drilling parallel to the axis is attempted, care must be taken to discard drillings until the drill is through the drag. In drilling from a surface that has not been sheared, a generous discard is also required, and the drillings reserved for the sample are taken from a location to represent the average composition of the metal between the center and

a side of the billet or bloom, as indicated by the illustration for large bars and shapes given in a succeeding paragraph. As a precaution against contamination from oil or grease, such drillings are thoroughly washed with clean ether and dried before beginning an analysis. Of the two methods, milling and sawing, the latter is superior for all steels up to a certain maximum hardness, and has been used successfully on slowly cooled sections containing up to 1.20 per cent carbon. The saw used is power driven with adjustable automatic feed,\* and is suitable for sections of all sizes up to 4 × 4-inch billets. The saw itself is extra thick and has teeth set to give a wide, free cut. It is made of high-speed steel and is 14 inches long, 1½ inches wide, 0.065 inch thick, with 4 teeth per inch. This saw gives cuttings 8 to 40 per cent of which are coarser than No. 10 sieve size with 2 to 5 per cent finer than No. 60 sieve size. After the saw has been used for a time, it gives slightly more fines. The method requires that the surface of the billet be thoroughly cleaned of scale and any other foreign material.

#### SAMPLING OF FINISHED MILL PRODUCTS

The term "finished mill products" includes all products as delivered by or from a mill, either for further processing and fabricating, or for placing in actual service. These are classified and treated as follows:

##### Number of Samples

In sampling finished materials, it is obvious that a single sample taken from one piece cannot be accepted as representative of a lot made up of a number of pieces, nor even of the piece from which the sample was taken, if the sampling was done carelessly. The number of pieces that should be sampled from a given lot or shipment depends upon the size of the section or weight of the single pieces, the tonnage or different melts involved, and the class or type of steel. Three samples taken from large sections may be more representative of ten tons, for example, than six samples of wire, though the latter weighs only a half ton. Not less than two samples can be taken as representative of a single piece unless it is very short or weighs less than 100 pounds, and at least three samples should be taken from any lot of three to ten pieces. For lots of more than three pieces, the number of samples taken will depend on the accuracy desired. Unless the steel is absolutely uniform, the accuracy will largely depend upon the number of pieces sampled. Also, the accuracy necessary depends on the source of the material. If the steel has been obtained from a careful and conscientious manufacturer, sampling of the finished product is unnecessary except when mixing of different grades in handling or errors in marking for identification are suspected. In gen-

\*The machine used up to the time of this publication has been manufactured by Racine Tool and Machine Company, Racine, Wisconsin.

eral, rules governing the number of samples to be taken for check analysis are:

1. Each melt or heat in a lot or shipment must be considered separately.

2. The number of pieces selected and analyzed from each melt should be sufficient to give an average analysis fairly comparable with the ladle analysis.

3. The pieces taken for analysis from each lot or shipment must be selected to represent each heat or melt as fairly as possible.

4. When the material is supplied to tensile test requirements, the samples for check analysis are taken from the tensile test specimens.

5. Some classes of materials are subjected to certain operations and processes which change the composition of the steel, or make it difficult to obtain samples which properly represent its original composition. Therefore, such materials should be sampled in the condition in which they were received from the manufacturer, or in the condition normal to them before they are subjected to such operations or processing.

Rods, small bars, small shapes, and wire are sampled by milling a complete cross-section from the end after all foreign matter of any kind has been cleaned from the surface. Rod and wire offer a special problem in that these sections are difficult to support properly during the milling operation. The principles of the devices employed are illustrated by the sketch of Fig. 4.

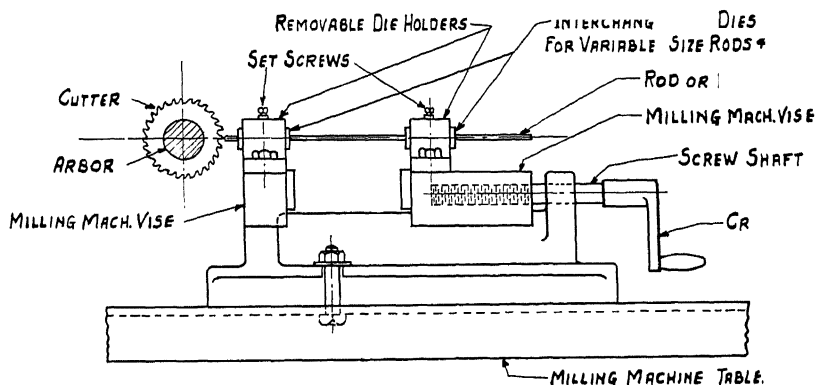


FIGURE 4. Apparatus for sampling rod and wire as devised and used by National Tube Company and American Steel and Wire Company.

Large bars and shapes are sampled by drilling parallel to the long axis from a point midway between the center and an edge of squares or the surface of rounds. If drilling parallel to the long axis is not practicable, the material is sampled by drilling through the piece at

a point midway between one edge and the center of the piece as a whole, as illustrated for bars and angles in Fig. 5; or by drilling to a depth short of the center, as shown by the dotted lines in the round

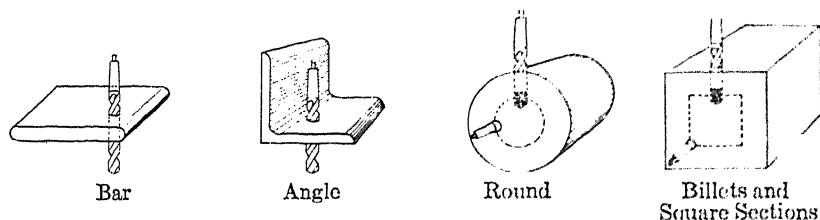


FIGURE 5. Proper location of drill holes in sampling large sections. Drill holes are represented by solid lines and circles are in accordance with Manufacturers' Standard Practice, which also permits drilling as shown by the dotted lines.

and square sections of the same figure. First drillings, of course, must be discarded, unless a clean surface is presented at the point of sampling. In addition, discarding of drillings to a depth of one inch or more when drilling large hot-sheared sections parallel to the axis is necessary to penetrate the "drag" left by the shear.

The reasons for these regulations are illustrated by Fig. 6. Although the position of the segregated area varies in different pieces and for different kinds of steel, and may not exist in many instances, let it be

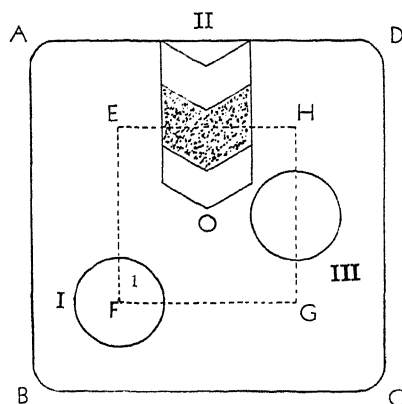


FIGURE 6. Illustrating how the composition of samples taken in different ways from a large square section may be affected by segregation.

assumed that ABCD is a 2-inch square and that all segregation lies within the small 1-inch square, EFGH. The area of ABCD is 4 square inches and that of the segregated portion 1 square inch. Hence, it is evident the sample should consist of 3 parts of drillings from the area, ABCD-EFGH, and 1 part from EFGH, and this is the propor-

tion obtained by sampling at I, the angle, 1, being  $90^\circ$  and the sector, 1, one-fourth of the area of the circle. From the first observation above, it is evident this location may not truly represent the section, but its advantages over drilling from II or from III are apparent. If the sample is taken as at II, drilling from the outside to the center, or as at III, drilling parallel to the axis to any depth, it will be made up of equal parts of drillings from the areas, ABCD-EFGH and EFGH, and will contain too large a proportion of drillings from the segregated portion. Also, it is very difficult to drill from the outer surface toward the center and gauge the depth so as to obtain a true proportion of all parts. For slabs and for square or rectangular sections larger than 6 inches, it is preferable to take cuttings at the center, O, at a half-way point on a diagonal, as at F and as near an edge, B, as practicable, analyze the cuttings from each point separately, and average the results. Two points, one at one-third and the other at two-thirds of the distance from the center to the surface, may give equally satisfactory results on sections of smaller size.

**Pipe and tubes** are sampled by drilling through the wall or by milling or sawing a section from the end. For seamless tubes, the exact location of the point of drilling is immaterial. Butt welded, lap welded, hammer welded, and electric welded pipe and tubes may give, for a certain element, one result if drilled through the seam and another if drilled through a point opposite the seam, for example. Therefore, sampling of the smaller sizes is preferably done by milling or sawing to obtain cuttings from a complete cross-section. Sampling of the larger sizes by milling or sawing is not practicable, and to obtain representative samples by drilling, standard specifications generally require that drillings for check analysis "shall be taken from several points around each tube selected for analysis," and the number of tubes selected for each lot of 250 lengths of boiler tubes (500 lengths of pipe) or of 2000 feet or fraction thereof shall not be less than two. (See A.S.T.M.-A83-36 and A53-36.)

**Strip** is sampled by cutting a full length of at least two inches in width from the end at right angles to the direction of rolling. This piece is thoroughly cleaned by pickling or grinding and is then folded flat upon itself at the middle to bring the 2 edges together, then refolded as often as desired, depending upon the width and gauge. The sample for analysis is taken by milling a uniform cut from the inside, or freshly cut, edges. If a full uniform section cannot be milled, or if it is necessary to drill the sample, the portion taken is located midway between the 2 ends of the folded piece. In dealing with strip in coils, at least one sample from each end of the coil should be taken, and the average analysis of the two samples considered as more nearly representative of the material than one sample taken by either of the methods described above.

**Sheets** are preferably sampled by taking a portion of the discard in shearing, to save material. If the sheet has been formed by cross-rolling from a bar, the discard sheared from the side of the sheet representing the full length and extending parallel to the direction of rolling is taken for the sample; but if the sheet has been formed by rolling in one direction only, the discards, sheared from the ends and representing the full width, are taken for the sample. In either case, the subsequent treatment of the specimen to obtain the sample for analysis is the same. The piece is thoroughly cleaned of all foreign material by pickling or other means. It is then folded flat at the middle, bringing the two ends together, and unless it is a very heavy-gauge sheet, it is folded a second time to bring the first fold over the two ends. The sample is then taken by milling from the sheared edge of the folded piece. These specimens are retained until material has been shipped and accepted by the customer. In sampling small sheets cut from larger ones, or any other sheet, the history of which cannot be traced to the ingot, it becomes a problem to determine from which edge a piece may be cut to represent the sheet as a whole. Analysis of the problem indicates the following procedure.

I. Cut strips from all 4 edges as illustrated in Fig. 7. Identify, fold, mill off sample, and analyze each edge separately.

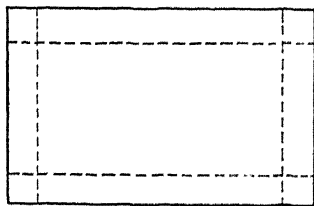


FIGURE 7. Diagram to illustrate the sampling of unknown sheets.

II. Compare the analyses and report results by combining analyses in accordance with deductions as follows:

(a) If the analyses of all 4 edges agree closely, the sheet is uniform. Report the average of the 4 analyses.

(b) If the analyses of opposite edges agree and adjacent edges do not, that is, if  $AB = DC$  and  $AD = BC$  and  $AB$  and  $DC$  differ from  $AD$  and  $BC$ , report the average of the 2 opposite edges giving the higher percentages of C, Mn, P, or S, etc.

(c) If the analyses of 2 opposite edges agree but the other 2 opposite edges do not, that is, if  $AB = DC$ , but  $AB$  differs from  $BC$ , report the average of the 2 opposite edges that agree.

# Qualitative and Quick Tests for Identifying Various Kinds of Steel

## Elements Common to All Steels

Of the many elements that may occur in steel, carbon, manganese, phosphorus, and sulphur are common to all steels. In addition, carbon steels frequently contain silicon and copper up to 0.30 per cent or more and may contain traces of such elements as aluminum, arsenic, antimony, chromium, molybdenum, nickel, nitrogen, oxygen, selenium, tellurium, tin, titanium, vanadium, zinc, and zirconium. Methods for determining the first group of elements have been improved to the point where it is quicker and cheaper to make a quantitative analysis than to attempt a qualitative test. In the case of the other elements in carbon steels, qualitative tests are not likely to reveal their presence, and the most exact quantitative methods must be resorted to in order to prove their presence or absence in the metal. In the hands of an expert, the presence of the elements occurring in small percentages is quickly revealed by examination of a sample with a spectroscope, but on account of its limitations, this method has not been generally adopted by the steel industry.

## Alloying Elements

Elements that are or have been added to steel for the purpose of controlling its properties, or for developing properties not possible by varying the proportions of the common elements, include aluminum, arsenic, beryllium, boron, chromium, cobalt, columbium, copper, molybdenum, nickel, selenium, silicon, tantalum, tellurium, titanium, tungsten, uranium, vanadium, and zirconium.

The corrosion and heat-resistant steels contain chromium; chromium and nickel; chromium, nickel, and silicon; chromium, nickel, and molybdenum; or chromium, nickel, and copper as the chief alloying elements. To improve the machining properties, increase the ductility, overcome intercrystalline corrosion, or increase creep strength, other elements such as columbium, selenium, titanium, vanadium, and zirconium are added. In other alloy steels, the elements most often encountered are aluminum, chromium, copper, manganese, molybdenum, nickel, silicon, titanium, vanadium, and zirconium, the use of cobalt, tungsten, and uranium being confined mainly to tool and other special steels.

Since the presence of one element may interfere with the determination of another by a given method, a preliminary test before proceed-



ing with the analysis of an unknown steel is desirable. Besides, much time may be saved in making complete analyses if the absence of certain elements can be proved by preliminary tests. The following tests have been devised to fill this need, as occasion may arise.

### QUALITATIVE TESTS

#### Tests Using a Single Sample

In developing the following tests, the object was to provide a means of detecting as many elements as possible with the use of but a single sample, thus saving time and conserving the sample, which may be limited.

#### Apparatus

The simple apparatus required is shown, connected for a test, in the accompanying diagram of Fig. 8, and requires no explanation.

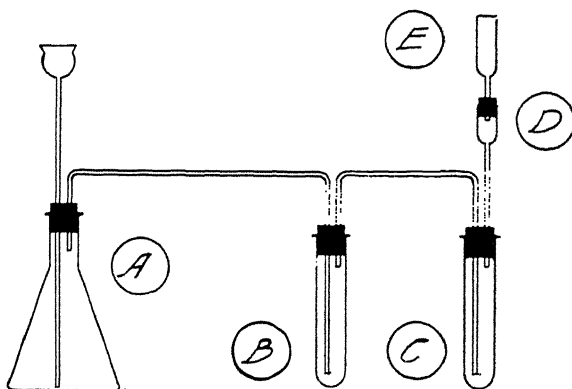


FIGURE 8. Apparatus for initial solution of the sample in a qualitative test of steel.

#### Solutions Required

Zinc Chloride Solution		
Zinc chloride	$\text{ZnCl}_2$	15 g
Potassium chloride	KCl	50 g
Water	$\text{H}_2\text{O}$	1000 ml
Hydrochloric acid	HCl	1.5 ml
Lead Acetate Solution		
Lead acetate	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	10 g
Water	$\text{H}_2\text{O}$	1000 ml
Acetic acid	$\text{CH}_3\text{COOH}$	Enough to clear up solution
Mercuric Chloride Paper		
Mercuric chloride	$\text{HgCl}_2$	5 g
	$\text{H}_2\text{O}$	1000 ml

Cut strips of filter paper 10 mm wide and 150 mm long. Dip the strips of filter paper into the  $\text{HgCl}_2$  solution and then place them on clean blotting paper to dry. Use the dry paper.

All reagents must be free from arsenic. A test should be run using pure zinc in place of a steel sample. If this test does not produce a yellow color on the mercuric chloride paper, the reagents can be safely used.

### Procedure

Set up the apparatus as sketched in Fig. 8. Transfer 2.5 to 5 g of the sample to flask A, about 20 ml of a slightly acid solution of  $\text{ZnCl}_2$  to tube B, about 20 ml of a slightly acid solution of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  to tube C, a plug of glass wool moistened with  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  solution to tube D, and a strip of filter paper impregnated with the  $\text{HgCl}_2$  solution to tube E.

**Test for Selenium, Sulphur, and Arsenic.**—Add 50 ml of dilute hydrochloric acid (1:1) to flask A, and apply a gentle heat to dissolve the steel. As soon as the sample has completely dissolved, heat the solution in flask A to boiling and boil until the tube connecting flask A and tube B becomes hot. The selenium will be retained in tube B, the sulphur in tube C, and the arsenic will pass through to tube E as arsine,  $\text{AsH}_3$ .

If the paper in tube E is colored yellow, arsenic is present.

The sulphur will be precipitated in tube C as brownish black  $\text{PbS}$ .

Add 10 ml of a 3-per cent solution of hydrogen peroxide to tube B. If selenium is present, a red precipitate will form.

**Test for Chromium.**—Transfer the contents of flask A to a 600-ml beaker and add 30 ml of 60-per cent perchloric acid,  $\text{HClO}_4$ . Evaporate the solution on a hot plate until fumes of perchloric acid are given off, and fume for five minutes to make sure that oxidation is complete. Remove the beaker from the hot plate and let it stand until cold. The residue in the beaker will crystallize and will have a red color if a large percentage of chromium is present. The color will be less pronounced as the proportion of chromium decreases. A faint pink color is produced by 0.06 per cent chromium. If no chromium is present, the residue will be white. The presence of tungsten will mask the color when but small percentages of chromium are present.

**Test for Silicon, Tungsten, Columbium, Tantalum, Zirconium.** Dissolve the residue in the beaker in 250 ml of water, heat to boiling, and boil for five minutes. Observe the precipitate. A yellow precipitate shows the presence of tungsten. A white precipitate indicates high silicon, columbium, or tantalum, or all three. In any case, if a precipitate has formed, filter it off and reserve the filtrate (filtrate A). Wash the precipitate with cold water, transfer the filter and contents

to a platinum crucible, and burn the filter paper. Add a few drops of sulphuric acid and a small amount of hydrofluoric acid to the crucible and evaporate to dryness. Ignite to a red heat. If the precipitate has completely volatilized, only silicon is present. In the absence of tungsten, a white residue indicates columbium, zirconium, or tantalum, or all three. In the presence of tungsten, treat the residue with ammonia or phosphoric acid to dissolve the tungstic acid. If the residue is dark colored, due to the presence of iron, fuse with a little sodium or preferably potassium pyrosulphate, dissolve in 50 ml of water, add 2 ml of hydrochloric acid, dilute to 250 ml with water, and boil for 5 minutes. A white precipitate will form if columbium or tantalum is present. Also, any tungsten present will be precipitated in whole or in part, and the solution will contain any zirconium precipitated on evaporation with  $\text{HClO}_4$ . To test for the latter, filter, add 10 per cent (by volume) of  $\text{HCl}$  to the filtrate and 5 to 10 ml of a 2-per cent solution of phenylarsonic acid, and boil. A white precipitate indicates zirconium, but the absence of a precipitate does not prove the absence of zirconium. Filter and reserve this solution for tin and test as directed later.

**Test for Titanium and Vanadium.**—Add 10 ml of hydrogen peroxide (3-per cent) to filtrate A and boil for 10 minutes. Cool and place 10 ml of the solution in each of 2 test tubes. Add 2 ml of phosphoric acid to each test tube, and then 10 ml of hydrogen peroxide to one tube and 10 ml of water to the other. A brown color in the test tube to which the hydrogen peroxide has been added indicates titanium or vanadium or both. Add a few drops of hydrofluoric acid to the brown solution. If the color is completely destroyed, only titanium is present. If it does not change, only vanadium is present. If the color fades but is not completely destroyed, both titanium and vanadium are present.

**Test for Cobalt and Nickel.**—Divide the remainder of the solution into 3 equal parts. Mark them solutions B, C, and D, respectively. To solution B, add an excess of zinc oxide. Allow the precipitate to settle and decant 10 ml of the supernatant liquid through a filter paper, collecting the filtrate in a test tube. Add crystals of potassium sulphocyanide ( $\text{KSCN}$ ) to the test tube so that the concentration will be about 30 per cent. Now add 10 ml of acetone. If cobalt is present, the solution will be colored blue.

Filter the remainder of solution B into a 250-ml beaker, and add 15 ml of hydrochloric acid and 2 ml of acetic acid to the filtrate. Neutralize with ammonia and add 5 ml of a 1-per cent alcoholic solution of dimethyl glyoxime. If nickel is present, a red precipitate will form.

**Test for Molybdenum and Copper.**—Heat solution C to boiling and pass hydrogen sulphide gas. A black or brown precipitate indicates copper or molybdenum or both. Filter and wash with hydrogen

sulphide water. Burn the precipitate at  $500^{\circ}$  to  $525^{\circ}$  C. Digest with 5-per cent solution of sodium hydroxide. If the precipitate dissolves completely, only molybdenum is present. If it does not all dissolve, decant the sodium hydroxide solution through a filter paper into a small beaker, allowing the precipitate to remain in the bottom of the crucible. Reserve the filtrate. Add nitric acid to the residue in the crucible and heat to dissolve the copper oxide. Transfer to a small beaker and add an excess of ammonia. If copper is present, the solution will be colored blue.

If molybdenum is present, it will be in the alkaline filtrate and should be confirmed. Acidify with dilute sulphuric acid (1:1), add 1 ml of 5-per cent solution of stannous chloride and a little potassium sulphocyanide. A red color will develop if molybdenum is present.

**Test for Zirconium.**—Make solution D neutral with HCl and add 10 per cent by volume in excess. Then add 10 ml of  $\text{H}_2\text{O}_2$  (3-per cent), follow with 10 ml of a 2-per cent solution of phenylarsonic acid, and boil one minute. A precipitate indicates zirconium.

**Test for Tin.**—Filter the solution from the phenylarsonic acid precipitate and combine the filtrate with that from the zirconium in the insoluble residue. Neutralize the solution with ammonia, add one per cent of HCl, and boil. Any tin present will be precipitated.

### Qualitative Tests Using Separate Samples

#### Procedure

Dissolve 0.5 g of sample in 15 ml dilute  $\text{H}_2\text{SO}_4$  (1:2), add 3 ml  $\text{HNO}_3$ , and evaporate to fumes. Cool, add 50 ml  $\text{H}_2\text{O}$ , warm, and filter off  $\text{WO}_3$ , if present. Add 1 g  $\text{Na}_2\text{O}_2$  to 50 ml of a 5-per cent solution of NaOH, pour the steel solution into it, boil 10 minutes, and filter through asbestos. Reserve precipitate for Ti and Zr. Test the filtrate as follows for:

**Chromium.**—A yellow-colored filtrate indicates chromium, which can be roughly estimated by diluting to a definite volume and comparing with standard alkaline solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{K}_2\text{CrO}_4$ , sensitive to about 0.1 per cent Cr.

**Vanadium.**—Acidify filtrate with  $\text{HNO}_3$ , adding 10 per cent excess. Then add 3 ml  $\text{H}_2\text{O}_2$ .

The yellow color will change to blue, then a faint green if chromium is present, and finally to a brown if vanadium is present; sensitive to about 0.05 per cent V.

**Titanium.**—Dissolve the NaOH precipitate in 50 ml hot  $\text{H}_2\text{SO}_4$  (1:10) and add 3 ml  $\text{H}_3\text{PO}_4$ . Take one-fourth of this solution and test for Ti with  $\text{H}_2\text{O}_2$  as described above for V.

**Zirconium.**—To the remainder of the solution of NaOH precipitate, add one g of diammonium phosphate, and digest on a steam bath for 2 or 3 hours. A white flocculent precipitate indicates the presence of zirconium.

**Cobalt.**—Dissolve 1 g of sample in 50 ml HCl (1:1). Add 3 ml HNO<sub>3</sub> and boil down to a syrup. Take up in 15 ml HCl (1:1) and filter on fritted glass, if necessary to remove insoluble matter, but do not wash. Transfer filtrate to separatory funnel, and extract iron with ether. Boil the lower acid solution and add a few drops of HNO<sub>3</sub>. Add a slight excess of NH<sub>4</sub>OH and filter.

In the absence of copper and nickel, a pink filtrate indicates cobalt. If copper or nickel is present, the solution may be blue, though the colors from cobalt and nickel tend to neutralize each other.

If the color is blue, acidify with HCl, pass H<sub>2</sub>S, and filter. Boil the filtrate till free of H<sub>2</sub>S, add 10 ml of alpha-nitroso-beta-naphthol (1.5 g dissolved in 10 ml of hot 75-per cent acetic acid), and boil 2 minutes. A red precipitate indicates cobalt.

To confirm, filter, ignite the precipitate in a clean porcelain crucible, and digest with 0.5 to 1.0 ml of HCl. Note color and add an excess of NH<sub>4</sub>OH. If cobalt is present, the acid solution will be blue and the ammoniacal solution pink.

## QUICK TESTS FOR IDENTIFYING STEELS

### Tests for High-Sulphur Steels

Provided a small section of flat surface can be properly prepared, two tests are available for distinguishing high-sulphur from low-sulphur steels. These tests, both used 20 to 25 years ago, are known as the sulphur print test and the arsenic test.

#### Arsenic Test

To make the arsenic test, clean a section of the steel of scale and smooth it with a file and emery cloth or a grinding wheel. Then, apply a fixed quantity (0.3 to 0.5 ml) of a standard dilute hydrochloric acid solution of arsenious chloride to the clean surface and observe the spot closely for a given time.

The H<sub>2</sub>S generated reacts with the arsenious chloride to form the yellow sulphide. With practice, the observer is soon able to distinguish between steels containing less or more than 0.050 per cent sulphur.

#### Print Test

To make this test successfully, a clean, smooth, flat surface is desirable. After the surface has been prepared, the test is made very quickly as follows:

Cut a small square (say 1 inch square) of No. 1 soft Azo photographic paper and soak it 2 minutes in dilute hydrochloric acid (1:4). apply the paper face down to the polished surface of the steel, cover it with blotting paper, press it gently to remove the excess acid, permit it to remain 2½ to 3 minutes. Then remove the paper and com-

pare the depth of the stain with prints similarly prepared from steels of known percentages of sulphur.

To make the prints permanent, they are fixed in "hypo" solution, washed, and dried.

### **The Smear Test for Nickel**

This test is applicable to billets, bars, sheets, plates, and many other forms of nickel steels soluble in nitric acid.

Clean a small area free of scale or any other foreign substance and apply 2 or 3 drops of  $\text{HNO}_3$  (1:1). After action ceases, absorb the solution with a piece of filter paper, and immediately apply to the wet spot on the paper 1 or 2 drops of dimethyl glyoxime solution. If nickel is absent, the spot will turn brown; if nickel is present, it will become red; sensitive to about 0.2 per cent nickel.

### **Quick Test for Titanium and Vanadium in Stainless Steels**

As titanium is one of the elements added to stainless steel, particularly the 18-8 type, to overcome intercrystalline corrosion, and since a minimum proportion in excess of about 0.30 per cent is required to obtain the desired effect, the following quick test for the detection of this element has been devised.

### **Procedure**

Transfer 0.2 g of sample to a small beaker, add 12 ml of  $\text{H}_2\text{SO}_4$  (1:1), and heat gently till solution is complete. Dilute if necessary, add 1 ml  $\text{HNO}_3$  (sp. gr. 1.42) drop by drop, and boil off nitrous fumes. Dilute to 50 ml, add 2 ml  $\text{H}_3\text{PO}_4$  (sp. gr. 1.71), and divide solution equally, transferring to two Nessler or other comparison tubes. To one tube, add 5 ml of  $\text{H}_2\text{O}_2$  (3-per cent) and 5 ml of  $\text{H}_2\text{O}$  to the other. Mix and compare colors.

If 0.1 per cent or more titanium is present, the solution to which the hydrogen peroxide was added will develop a yellow tint if vanadium is absent, brownish if vanadium is present.

Add 1 to 2 ml of hydrofluoric acid, or preferably 5 ml of a 10-per cent solution of  $\text{NaF}$ , to the yellowish solution and mix.

The yellow color will fade out completely if only titanium is present, but will become a darker brown if vanadium is also present.

# Methods of Analysis

## General Remarks

In compiling this book, many topics usually discussed in works on analytical chemistry have been omitted. These include such subjects as laboratory equipment; purity of reagents; accuracy of weights and volumetric glassware; effect of reagents upon platinum, porcelain, and glassware; safe handling of reagents and chemicals; effects of dust and other impurities in the air of the laboratory; cleaning agents; care of apparatus; and many others, all of which it is assumed have been part of the education of the well-trained analytical chemist in charge of the work. However, we add the blanket specification that all reagents, including distilled water, should be of highest purity; weights and volumetric glassware should be of highest practicable accuracy, and special apparatus should be the same as described in the methods; also, it appears desirable to call attention to the following:

**Caution in the Use of Perchloric Acid.**—Throughout this book, the use of perchloric acid has been prescribed whenever its use seemed advantageous. The acid is an energetic oxidizing agent, and, on this account, its use is attended not without a certain hazard from fire and explosions. Some laboratories have used the acid for years without mishap, but others have experienced troubles. In its most concentrated form (70 to 72-per cent), it should be kept in a dark, cool, and safe place, not on a shelf but on floor level, where there is no chance of a container being broken. In diluted form (55-per cent), it is handled with comparative safety. In hot concentrated form, it reacts violently or explosively with many organic and some high-sulphur compounds. Most of the determinations in which it is used require heating to the fuming stage. Apparently, the vapors that escape into the air condense on the walls of hoods and ventilators, where they react with wood and other oxidizable materials to form easily ignited parts and deposits liable to spontaneous combustion. Therefore, hoods in which this acid is frequently used should be cleaned regularly, all parts including the ventilator ducts being well washed and rinsed with water.

**Concentration of Solutions.**—Following long custom, the concentrations of dilute solutions only are given, and are expressed in terms of specific gravity, per cent by volume for liquids or by weight for solids, or in terms of a ratio showing the parts by volume of liquids to the parts by volume of water. When the dilution is not given, it is understood that the concentrated reagent as supplied by the manufacturer is intended. When a reagent not manufactured or supplied

to a standard concentration is specified, the lowest concentration permissible in the method is designated.

**Use of ml instead of cc.**—In dealing with the measurement of volumes, we use ml instead of cc to correspond to the manufacturers' system of marking glassware and to comply with recommendations of the Bureau of Standards and authoritative definitions of the terms milliliter and cubic centimeter.

A milliliter (1 ml) is 1/1000 of a liter, which is defined as the volume of 1 kilogram of water at 4° C. Since 4° C. is too low for working room temperatures, efforts, started about 1922, led to the adoption of a working standard referred to 20° C, which included corrections for the expansion of glassware from 4° C to 20° C. Hence, 1 ml means a definite volume measured at 20° C, and all volumetric glassware is so marked.

A cubic centimeter (1 cc) is 1/1,000,000 of a cubic meter, and, since the meter is a definite length, it is a definite volume without reference to the effect of temperature upon liquids or containers.

### Elements that may Occur in Steel

Since the determination of each element, with but few exceptions, is made on a separate sample, and, therefore, forms a separate section, the official order for reporting the elements has been followed in arranging the methods for their determination, which is as follows: C, Mn, P, S, Si, Cu, Ni, Cr, V, Mo, Ti, Al, As, Sn, Co, W, U, Zr, Cb, Ta, Se, Sb, Zn, B, Be, N, O, and H.

To this list of 28 elements should be added lead, possibly fluorine, some of the alkalies and alkaline earths, and iron itself; for in many of the high-alloy steels, iron may constitute less than 70 per cent of the metal, and its separation becomes a problem in the determination of elements which cannot be selectively separated from other components of the steel or determined in the presence of iron.

In this book are given methods for the determination of all these elements, except the alkalies and alkaline earths, and two of the gaseous elements, oxygen and hydrogen, for which no reliable methods applicable to all kinds and types of steel have been developed.

## DETERMINATION OF CARBON

### Methods

A great many methods have been developed for the determination of this element. Classified according to fundamental principles they are as follows:

1. Estimation by inspection of a fractured surface of a sample treated in a certain way.
2. Estimation by some form of hardness testing.
3. Solution of the sample in a mixture of chromic and sulphuric



acids. The carbon, oxidized to  $\text{CO}_2$  by the mixture, was collected and estimated in various ways.

4. Solution of the sample in dilute nitric acid and estimation of the carbon by color of the solution. Developed in 1862 by Eggerts, this method is still used to a limited extent, but is not applicable to alloy steels, and requires a set of standards for each kind of steel with standards and test samples prepared in exactly the same way.

5. Solution of the sample in cupric sulphate and oxidation of the residue in a mixture of chromic and sulphuric acids.

6. Solution of the sample in a solution of potassium- or ammonium-copper chloride, the residue being filtered off, washed, and weighed.

7. Solution of the sample in a solution of potassium- or ammonium-copper chloride, followed by combustion of the residue in air or oxygen, the  $\text{CO}_2$  formed being absorbed and determined volumetrically or gravimetrically.

8. By volatilization of the iron in a current of hydrochloric acid followed by combustion of the residue in air or oxygen.

9. By volatilization of the iron in a current of chlorine followed by combustion of the residue in air or oxygen.

10. Ignition of the finely divided sample with a mixture of lead chromate and potassium chlorate, the evolved  $\text{CO}_2$  being collected in KOH and weighed.

11. By direct combustion of the sample in a current of oxygen, the  $\text{CO}_2$  evolved being absorbed with alkaline reagents and measured volumetrically, weighed directly or as barium carbonate, or estimated directly or indirectly by titration. This method has been developed to a high state of perfection and with the latest improvements represents the quickest and at the same time the most accurate method ever devised for the determination of carbon in ferrous materials.

12. Microscopic methods in which the carbon is estimated by microscopic examination of a specially prepared surface.

13. Spark testing is very old. In the early days, the steel was "struck" with flint. Recently, special grinding wheels have been used for the test which, in conjunction with carefully prepared standards, make it possible to estimate the carbon within 2 to 10 points, or 0.02 to 0.10 per cent, depending upon the grade and type of steel being tested and the skill of the tester.

14. Electrical resistance, or the Enlund Method, depends upon the rule first stated by Benedicks that elements dissolved in iron increase the specific electrical resistance by an amount inversely proportional to their atomic weights, and upon the fact that carbon can be held in or thrown out of solid solution at will by quenching or cooling slowly. The difference in the specific electrical resistance between a properly prepared and quenched specimen and the same or a similar specimen annealed or normalized gives a factor which can be translated into per cent carbon, while the total resistance of the former gives the

effect of all the alloying elements in the steel. If other alloying elements are absent, the method also permits the determination of manganese, or of silicon, if the manganese is known. Also, the tensile strength, and the hardness of some steels, is obtained by the application of a proper factor to the specific electrical resistance of the quenched specimen.

15. The magnetic method depends upon the fact that the incremental permeability of steel as measured by deflection of a ballistic galvanometer is proportional to the carbon content. Alloying elements other than carbon have a similar effect, hence its use is restricted largely to the preliminary testing of plain-carbon steels made in the open hearth or the bessemer process. Determinations are made with a special instrument, called the "carbometer," which must be calibrated by comparing readings with carbon results by chemical analysis on the same specially prepared test specimens.

## Combustion in Oxygen

### Introductory Remarks

For all kinds and types of steel, carbon is determined most rapidly and accurately by direct combustion in oxygen. During the 20 years this method has been in general use, many variations in apparatus and procedure have been introduced to meet the ever increasing requirements, the latest development being modifications to permit the determination of both carbon and sulphur simultaneously.<sup>1</sup> With carbon steels, all these variations may be permissible, but with the class of steels herein dealt with many of them must be discarded as failing to give the conditions necessary to obtain correct results. Again, it is true that with proper equipment assembled to give the required conditions, the procedure is very simple; but the knowledge, skill, and experience of an expert are required to assemble suitable apparatus, select proper reagents, and arrange for the combination to function efficiently and give accurate results. In such hands, various modifications in the method are possible without affecting the accuracy.

### Limits of Accuracy for Carbon by This Method

In routine and commercial analyses, particularly of the higher-carbon steels, a variation of 0.02 per cent in results from different laboratories is to be expected, but results on the same sample in the same laboratory should check within 0.01 per cent. In referee work, a tolerance of  $\pm 0.005$  per cent from the average of the closely agreeing results is permissible, because the limit of accuracy, also the limit of reproducibility of the method for any kind of steel is about  $\pm 0.003$  per cent. In analyzing steels containing less than 0.05 per cent carbon and alloy steels of the class herein treated, this limit of accuracy must be closely approached.

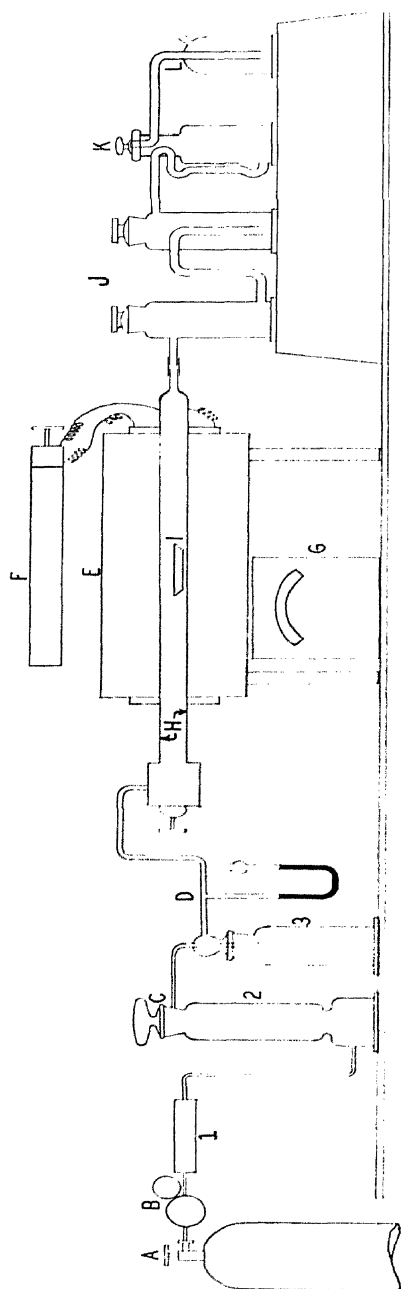


FIGURE 9. Diagram of combustion train for the determination of carbon in highly alloyed steels.

## **Apparatus and Reagents**

The essential parts of the apparatus used for the determination of carbon are illustrated diagrammatically in Fig. 9. These parts and the reagents that may be used are listed and briefly described, with reference to the symbols used in the drawing, as follows:

**A. Oxygen Supply.**—Compressed or liquid. Preferred 99.5 per cent  $O_2$ , free of  $CO$ ,  $CO_2$  or any other acidic gas or carbon-bearing material. If oxygen of this grade cannot be obtained, special provision must be made in the train to purify it as noted below.

**B. Pressure Reducing Valves.**—The valve or valves used to regulate the pressure of the escaping oxygen must be capable of stepping down the pressure from the oxygen supply to not more than 2 pounds and permit a steady flow of oxygen through the train. Several different types of valves or pressure reducing regulators suitable for the purpose are manufactured and are readily obtainable. A system or regulator that reduces the tank pressure in two stages is preferable.

**C. Oxygen Purifying Train.**—With oxygen of a purity specified above, there is no need of a purifying train. However, as a precaution, it is customary to insert a  $CO_2$  absorbent, such as soda lime, sodium or potassium hydroxide in solid form, or a solution of these followed by calcium chloride. As a guard against other carbon-bearing fluids, sulphuric acid followed by potassium hydroxide solution and calcium chloride has been used, the acid being renewed when it becomes discolored. Some of the best analysts, however, avoid the use of liquids in this or any other part of the train. But if the highest grade oxygen is not used, this part of the train must provide for the combustion of all carbon-bearing matter and the subsequent absorption of the  $CO_2$  as shown in the diagram. To effect combustion of impurities, an electrically heated tube, C-1, is provided. This tube is lightly packed with ironized asbestos or copper oxide and heated to a temperature of  $600^\circ C$  to  $650^\circ C$ , following which the  $CO_2$  and other acidic gases are absorbed with soda lime or potassium hydroxide solution in a suitable container, C-2. If the latter is used, it must be followed by an efficient dehydrating agent such as fused calcium chloride in a drying bottle, C-3.

**D. Mercury Trap or Manometer.**—A mercury trap is preferred by some as it serves not only to indicate the pressure roughly, but also prevents backflow of gas.

**E. Electric Furnace.**—A furnace capable of giving temperatures from  $1050^\circ C$  to  $1400^\circ C$  is desirable. For most carbon and low-alloy steels, a temperature between  $1000^\circ C$  and  $1100^\circ C$  is satisfactory, if a suitable accelerator, as explained later, is mixed with the sample.

It has been stated<sup>2</sup> that a high temperature causes the steel to melt rapidly and trap some carbon monoxide, and that temperatures above  $1150^\circ C$  are apt to result in the reduction of some of the carbon dioxide

before it can be driven from the region of the boat. Members of this committee have experimented with temperatures as high as  $1400^{\circ}\text{C}$ , but low results due to these causes have not been observed with a  $1\frac{1}{2}$ -inch or larger tube and with oxygen supplied at a sufficiently rapid rate. Economy and convenience both influence the operator to use no higher temperatures than are necessary.

The high-temperature furnace should operate on 110 or 220 volts, A.C. or D.C. current. New furnaces should be heated slowly to the operating temperature, as very rapid heating may cause the refractory to crack and spall from the outer insulation. Low-temperature furnaces for operating below  $1100^{\circ}\text{C}$  are generally wire-wound, and are best operated at low voltages requiring A.C. current and a transformer.

**F. Rheostat.**—A high-temperature furnace of the type specified above requires only a rheostat to control the temperature within operating limits. With proper attachments, it is possible to make this control automatic, and such control is recommended wherever the amount of work to be done will justify the initial expense. When the voltage varies considerably, constant voltage regulators are available.

**G. Pyrometer.**—To operate a furnace without automatic temperature control, a pyrometer is necessary, as temperatures above  $950^{\circ}\text{C}$  fall within the white-heat range and cannot be judged closely by eye. The hot junction of the thermocouple should be located within the heating chamber of the furnace and as near the combustion tube as possible. With low-temperature furnaces, a pyrometer is not necessary, except for checking the eye readings occasionally. An optical pyrometer may be used for checking the temperature by focusing on the end of the boat.

**H. Combustion Tube.**—The tube must be made of material that will remain gastight and nonsoftening at the temperatures and pressures used, and not absorb  $\text{CO}_2$  at any temperature. For high temperatures, a tube of unglazed vitrified clay or porcelain is preferable, though some brands of fused quartz tubes have been successfully used with temperatures up to  $1200^{\circ}\text{C}$ . As to size,  $1\frac{1}{2}$  inches I.D.  $\times$  28 inches is best, all factors considered. The exit end is preferably reduced in diameter to permit connections with rubber tubing. The end of the tube remains much cooler if this reduction is in two steps. The inlet end of the tube is best equipped with a metal breech connector. If a rubber stopper is used, it must be provided with a suitable shield against the heat, or the end of the tube should be water-cooled. In continuous operation at high temperatures, a packing of any kind in the tube is not necessary or desirable and is usually omitted. If provision is made to absorb the oxides of sulphur beyond the tube, no packing is used. When combustions are conducted at constant temperatures of  $1000^{\circ}$  to  $1050^{\circ}\text{C}$ , the exit end of the tube may be packed with ironized asbestos to remove the oxides of sulphur and selenium, but it is necessary to drive out these oxides by

drawing the tube back into the furnace and aspirating with oxygen after every 150 combustions of low-sulphur steel and oftener with high-sulphur steels.

**I. Boat and Lining.**—Boats made of porcelain, refractory clays, or sheet nickel are satisfactory. If nickel is used, the boat is formed from 18-gauge sheet, maximum carbon 0.02 per cent, and the boat is ignited, after forming, for 1 or 2 hours at  $950^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$ . If the boat is to be used at higher temperatures, it should be ignited at the combustion temperature until it gives no blank. The approximate size, outside dimensions, is  $\frac{3}{4}$  inch wide,  $\frac{1}{2}$  inch deep, and 4 inches to 6 inches long, with walls as thin as practicable.

The boat is lined with alkali-free alundum, 60-mesh to 90-mesh, or with highest grade chrome ore, crushed, sized, washed with hydrochloric acid and water, dried, and ignited. Other linings may be used provided they do not flux with iron oxide, in which case, the slag formed may retain bubbles of carbon monoxide and increase the splattering. Boats and lining material of whatever kind must be pre-ignited and kept protected from dust and other foreign matter before they are used. In practice, the boat is almost filled with the lining selected, a longitudinal groove is formed in the lining and the sample cuttings are placed therein, being spread along the groove or poured in a pile, as described later.

**J. Second Purifying Train.**—The functions of this part of the train are to remove dust, traces of water, oxides of sulphur and selenium, and all other acidic gases except  $\text{CO}_2$  from the excess oxygen before it enters the  $\text{CO}_2$  absorber.

#### *Removal of Dust, $\text{SO}_2$ , etc.*

In the analysis of low-sulphur steels, dust and the oxides of sulphur, selenium, and tellurium are all removed very efficiently by means of a tube packed lightly with finely divided and highly ironized asbestos. The asbestos is prepared by saturating well-shredded asbestos with a 10-per cent solution of ferrous sulphate, slightly acidified with sulphuric acid, then drying, and finally igniting at a temperature of  $1000^{\circ}\text{C}$  for 6 to 8 hours. The asbestos is followed by a dehydrating tube containing the same desiccant as is used in the  $\text{CO}_2$  absorber, the desiccant being one of the more efficient dehydrating agents recommended later. In the absence of selenium, various combinations for the removal of oxides of sulphur and water have been used with apparent success, some of which will also remove selenium. Some of these are: (1) glass wool, lead dioxide, zinc shot, and dehydrite. The use of either lead dioxide or zinc, however, is not recommended. (2) Precipitated neutral manganese dioxide followed by dehydrite, anhydron, or phosphorus pentoxide. (3) A 50-per cent solution of chromic oxide or a 5-per cent solution of potassium permanganate followed by concentrated sulphuric acid and anhydron. (4) A tube

containing chromic oxide in granular form followed by a saturated solution of chromic oxide in concentrated sulphuric acid and a tube of  $P_2O_5$  or of anhydrene,  $Mg(ClO_4)_2$ , is satisfactory, if the  $CO_2$  bulb contains  $P_2O_5$  or anhydrene, that is, the same desiccant as is used in the preceding tube. Liquids in the purifying train are not desirable, and of the solid absorbents the precipitated neutral manganese dioxide is especially recommended. It is prepared as follows:

*Preparation of Manganese Dioxide.*—For approximately 50 g of the manganese dioxide, 200 g of manganous sulphate,  $MnSO_4 \cdot 4H_2O$ , are transferred to a 4-liter beaker or flask and dissolved in 2.5 liters of water. This solution is made distinctly ammoniacal, 1 liter of a freshly prepared solution of ammonium persulphate containing 225 g of the salt is added, and the mixture is heated to boiling. Boiling is continued for 10 minutes, more ammonia being added from time to time as may be necessary to keep the mixture ammoniacal. The precipitate is allowed to settle, and if the supernatant liquid is cloudy, or if the precipitate does not settle quickly, 50 to 100 ml of the ammonium persulphate solution are added, and the boiling is continued for another 10-minute period with additions of ammonia as required. When it is apparent that precipitation is complete, the mixture is set aside until the manganese dioxide has settled thoroughly. The supernatant solution is carefully siphoned from the precipitate, which is then washed by decantation with 3 to 4 liters of hot water added in portions of 500 to 600 ml, the dioxide being well mixed with the water and allowed to settle well after each washing before the water is decanted. Finally, it is washed twice in the same thorough manner with water slightly acidified with sulphuric acid. In the meantime, a filter is prepared by fitting a 6-inch funnel with a 2-inch filtering disc and depositing thereon a thin mat of purified asbestos. Instead of these items a Büchner-type porcelain funnel may be used. After the last washing, the manganese dioxide is transferred to this filter and washed with hot water until it is free from sulphates. It is then transferred to a clean porcelain dish and dried in an oven at  $105^\circ C$  when it is ground in a mortar to pass a 20-mesh sieve, and again dried at  $105^\circ C$  until it is thoroughly dry.

*Preparation of the Manganese Dioxide Tower.*—To prepare the sulphur remover, a bottle such as that shown in Fig. 10 is used. It is packed and prepared as follows: Ironized or plain washed and ignited asbestos is first placed in the bottom and slightly tamped into place to a depth of  $1\frac{1}{2}$  inches. Upon this bedding, the manganese dioxide is poured in a small stream so as to keep the coarse and fine particles evenly distributed until the bottle is filled to within about 2 inches of the gas outlet. The top surface of the dioxide may be leveled by tapping the bottle lightly on the side, but it should not be tamped into place. Finally, the neck of the bottle is packed tightly with a plug of fine long-fiber cotton, or preferably fine fiber glass cotton, so

as to leave a space of about  $1\frac{1}{2}$  inches above the dioxide, and the bottle is closed with a rubber stopper. The packing, especially if glass cotton is used, may absorb some  $\text{CO}_2$  at first. To condition the bottle for service, it is placed in the combustion train next to the combustion tube and just ahead of the drying tower which precedes the

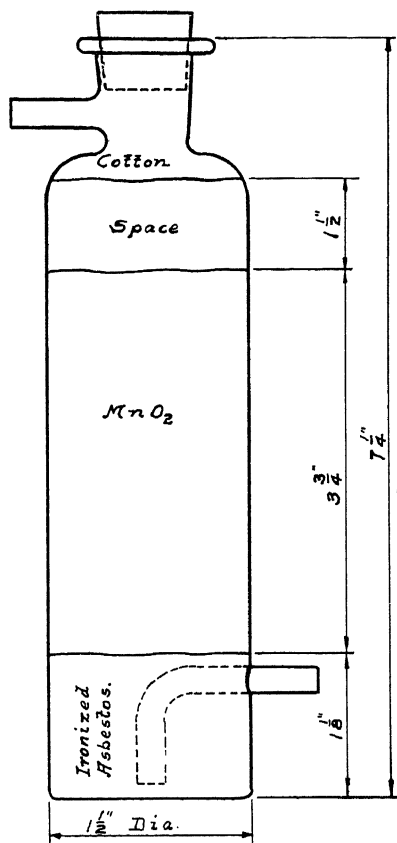


FIGURE 10. Tube charged with specially prepared manganese dioxide for removing oxides of sulphur from the gaseous products of combustion.

absorption bottle. Two blank determinations are made, using a high-carbon steel standard. If the carbon result is low, either a high-sulphur steel standard or the same standard with 12 mg of sulphur added is analyzed, and the blank with the original high-carbon standard is repeated. This treatment is prescribed because manganese dioxide is said to hold a little carbon dioxide by absorption, which is partly given off if the temperature is raised or if it is treated with gases containing no carbon dioxide. When the bottle has thus been conditioned, and the train is properly aspirated after each combustion, no noticeable



error due to this cause has been detected. One filling of the bottle lasts for several hundred combustions even if all the tests are made with high-sulphur steels and irons.

It is thought by some that the sulphur dioxide first reacts with the manganese dioxide to form manganese dithionate, thus:  $\text{MnO}_2 + 2\text{SO}_2 = \text{MnS}_2\text{O}_6$ ; others believe the reaction is,  $\text{MnO}_2 + \text{SO}_2 = \text{MnSO}_4$ , or that both may occur. Whatever the reaction, the manganese dioxide

TABLE 1. RESULTS OF TESTS OF DEHYDRATING AGENTS.<sup>a</sup>

Desiccant Tested * (Common or Trade Name)	Chemical Formula	Preparation For Use in This Test	Comparative Drying Efficiencies	
			Max. Vol. Air Dried (Liters per ml of Desiccant)	Residual Water in Air After Drying (Mg of $\text{H}_2\text{O}$ per liter of Air)
Copper Sulphate (Anhydrous)	$\text{CuSO}_4$	Dried 2 hrs. at $250^\circ$ C in air dried with $\text{P}_2\text{O}_5$	0.7	2.8
Calcium Chloride granular, 8 mesh	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$	Used as obtained	24.2	1.5
Calcium Chloride (Technical Anhydrous)	$(\text{CaCl}_2)_4 \cdot \text{H}_2\text{O}$	Used as obtained	5.8	1.25
Zinc Chloride, sticks, C.P.	$\text{ZnCl}_2$	Used as obtained	2.1	0.98
Desicchlora, Barium Perchlorate (Anhydrous)	$\text{Ba}(\text{ClO}_4)_2$	Used as obtained	3.7	0.82
Sodium Hydroxide, sticks, C.P.	$\text{NaOH}$	Crushed to a coarse powder	8.9	0.80
Calcium Chloride, granular, dehydrated	$\text{CaCl}_2$	Heated to $275^\circ$ C in air dried with $\text{P}_2\text{O}_5$	7.8	0.36
Dehydrite, Magnesium Perchlorate-Trihydrate	$\text{Mg}(\text{ClO}_4)_2$ $\cdot 3\text{H}_2\text{O}$	Used as obtained	7.2	0.031
Silica Gel	$\text{SiO}_2 + 11\% \text{H}_2\text{O}$	Heated to $130^\circ$ C in air dried with $\text{P}_2\text{O}_5$	7.7	0.03
Potassium Hydroxide, sticks	$\text{KOH}$	Crushed to a coarse powder	7.2	0.014
Hydralo, Aluminum Trioxide	$\text{Al}_2\text{O}_3$	Heated 6 hrs. at $150^\circ$ C to $180^\circ$ C in air dried with $\text{P}_2\text{O}_5$	7.7	0.005
Calcium Sulphate, (Anhydrous) ("Sol- uble Anhydrite")	$\text{CaSO}_4$	Used as obtained	18.5	0.005
Calcium Oxide, C.P.	$\text{CaO}$	Heated 4 hrs. at $650^\circ$ C, cooled over $\text{BaO}$	10.1	0.003
Anhydron, Magnesium Perchlorate (Anhydrous)	$\text{Mg}(\text{ClO}_4)_2$	Used as obtained	13.2	0.002
Barium Oxide	$\text{BaO}$	Used as obtained	25.0	0.00065
Phosphorus Pentoxide	$\text{P}_2\text{O}_5$	Used as obtained	?	Used as final
Sulphuric Acid, C.P. (Concentrated)	$\text{H}_2\text{SO}_4$	Used as obtained	?	absorbent Used as final

\* Materials listed in the order of their efficiencies.

in the sulphur remover gradually becomes white or very light in color, the change progressing from the bottom up as more and more sulphur is absorbed. Therefore, it is its own indicator as to when it is approaching exhaustion and should be renewed.

**Desiccants.**—A number of drying agents have appeared on the market, one of the most recent being sold under the trade name of "Drierite," which can be prepared with an indicator to change color as it absorbs moisture. From the standpoint of removing all the water from a gas, among the most efficient are phosphorus pentoxide and concentrated sulphuric acid. Results of Bower of the National Bureau of Standards are shown opposite in Table 1. The method employed for determining the comparative efficiencies of the materials tested, as stated by Bower, "was to aspirate properly conditioned air" (air containing a constant amount of moisture at 30° C) "through a train of U-tubes containing the drying materials in the order of their increasing drying powers. After a measured amount of air had passed through the system, the increase in the weights of the U-tubes following any U-tube indicated the residual water escaping that tube. No study has been made of the capacities of the materials or the limiting rates of air flow."

**K. CO<sub>2</sub> Absorption Bulb.**—Several types of bulbs for absorbing the carbon dioxide are in use, including those known as the Nesbitt, Muehlberg, Richards, Fleming, Miller, Midvale, and Vanier bulbs. All are acceptable, but closed types are recommended. The weight of the packed absorber should not exceed 200 g, to avoid overloading the balance, and another of the same kind should be used as a counterpoise in weighing.

The bulb, or bottle, is packed from the bottom up with glass wool, soda lime, or soda asbestos (Ascarite), a thin layer of asbestos, the same desiccant as is used in J above, and glass wool. Failure to include the desiccant will give low results. Ascarite and soda lime are recommended as absorbents for the CO<sub>2</sub>, and anhydrous or phosphorus pentoxide as the desiccants.

A newly packed bulb is first filled with oxygen to replace the air, then allowed to stand in the balance case at least 5 minutes, and weighed just before it is used. Variable temperatures may affect the weight slightly. Therefore, it is advisable to weigh at as near a constant temperature as possible, and if the bulb is light-weighted at room temperature, it should be allowed to stand after filling with oxygen until it reaches approximately the same temperature. When combustions follow in rapid succession, so that the heavy weight of one may be used as the light weight for the next combustion, it is not necessary to let the bulb stand before weighing. Therefore, some proceed as follows with newly packed bottles. First, the air is displaced with oxygen, then the bulb is attached to the train and a sample of

steel is burned as in a determination. The bottle is weighed and checked by running a standard sample of steel.

**L. Gas Flow Indicator.**—The functions of this part of the apparatus are to guard the absorber and indicate the gas flow from the train, which must not be permitted to cease during a combustion. Flow meters may be of the pressure gauge type, such as the Brown Flow Meter, or of the bubble type. As a rule, concentrated sulphuric acid is used in the latter.

### Checking the Train

After the train has been assembled ready for operation, it should be checked before use, and regularly thereafter, for leaks and blank. The blank is found by placing the boat, containing only the lining, in the tube and passing oxygen as in a determination. The train may not be used for routine work until the blank is 0.0005 g or less, and a correct result (within the tolerance of  $\pm 0.005$  per cent) is obtained on an authoritative standard sample. In referee work, 2 to 3 blank determinations, omitting only the sample in the boat, should be made prior to each determination to establish exactly the weight of the blank, which should be deducted from the weight of  $\text{CO}_2$  found. The blank is not constant, even when the materials are handled with the greatest care.

### Weight of Sample

To simplify calculations, some multiple of the factor  $0.2727 \left( \frac{\text{C}}{\text{CO}_2} \right)$  is used, usually 1.3636 g or 2.727 g, the latter for very low-carbon steels, and, in referee work, for those up to 0.6 per cent carbon. These weights are known as factor weights and are employed to avoid calculations and possible mistakes from this source. With 1.3636 g, 20 times the weight of the  $\text{CO}_2$ , or with 2.727 g, 10 times the weight of the  $\text{CO}_2$ , gives the per cent carbon. Also, a large sample of 4.09 g is recommended for samples containing less than 0.04 per cent carbon.

### Use of Accelerators with the Sample

Before high temperature furnaces were available, various substances called accelerators were added to the sample to effect complete combustion and liberation of all the carbon. With a high-temperature furnace, giving working temperatures of  $1200^\circ \text{C}$  ( $2200^\circ \text{F}$ ) or higher, the use of an accelerator is seldom necessary, except for certain high-alloy steels, when approximately 0.5 g of pure tin (20- to 40-mesh) is added to the sample in the boat. Tin has been proved the best material yet found for steels. With tin added to the sample, satisfactory results on most high-alloy steels are obtained by burning at temperatures between  $1050^\circ \text{C}$  and  $1100^\circ \text{C}$ . Magnesium ribbon has also been found suitable for use with steels, about 0.05 g being used with each

combustion. As the ribbon is about  $\frac{1}{16}$  inch wide and weighs about 0.0125 g per inch, four strips about 1 inch long are placed in the groove of the boat lining, and the sample is spread thereon. Ribbon  $\frac{1}{4}$  inch wide and heavier may be used, of course, with finer pieces.

With extremely highly alloyed metals, however, such as ferrochromium, tin alone fails, and it is necessary to add some iron to obtain complete combustion of the sample. For this purpose, hydrogen-reduced iron or a carefully standardized sample of commercially pure iron (2.727 g) is used.

### Fineness of Cuttings

As explained under sampling, the cuttings are generally sieved and those finer than 60-mesh are discarded, as giving high results for carbon, probably due to fine particles abraded from the cutting tool (drill, saw, or milling cutter). However, sieving of all samples may not be desirable, particularly those of high-carbon steels that have been obtained by milling, the fines of which may contain carbide components of the steel. With low-temperature furnaces, fine cuttings (20-mesh to 60-mesh) were desirable to promote complete fusions, but with higher temperatures, coarse cuttings, even chunks of carbon steels, can be burned as readily as fines. However, fines in the sample are a convenience in weighing and some highly alloyed steels are difficult to burn even with fine cuttings. Therefore, for the carbon determination, the portion of any sample obtained by drilling is sieved on a nest of a 10-mesh and a 60-mesh sieve, and the portion remaining on the No. 60 sieve is reserved for the carbon and other determinations in which fine cuttings are desirable.

### Gravimetric Method: Direct Weighing of $\text{CO}_2$

#### Procedure

With the train properly assembled and tested, the procedure is as follows: Weigh the  $\text{CO}_2$  absorber against its counterpoise. Fill a boat with the prescribed bedding material, and make a V-shaped groove or depression extending the full length of the boat. Weigh the proper factor weight of sample, and charge the boat as follows: with ferroalloys, add the iron accelerator first and spread the sample upon it. If tin is used as the accelerator, it is added on top of the sample of steel or of iron and the sample of ferroalloys. Now insert the boat into the end of the combustion tube. Using a clean rod or piece of stainless steel wire, push the boat forward 3 or 4 inches and let it warm up there for about 1 minute before pushing it into the hottest zone of the tube, this procedure being desirable with tubes sensitive to thermal shock. As soon as the boat has been pushed into position, close the tube and turn on the oxygen slowly till the flow is 300 to 500 ml per minute, depending upon the time available for a determination, the larger flow being used in routine work.

When magnesium ribbon is used as the accelerator, the following procedure is prescribed:

Place the magnesium ribbon (0.05 g) in the groove made in the bedding material of the combustion boat, add the sample, push the boat into the hot zone of the combustion tube, and immediately turn on the oxygen full. With magnesium, no preheating is permissible, as the magnesium ignites in 20 to 30 seconds, and in the absence of oxygen it will burn without igniting the steel. It is necessary to use additional iron only with small samples, such as high-carbon ferrochrome.

After the combustion of the steel has ceased, continue the flow of oxygen until all the  $\text{CO}_2$  has been swept into the  $\text{CO}_2$  absorber, a period which will vary with the rate of flow of oxygen and with the train. In routine work, with dry  $\text{SO}_2$  absorbers and ascarite as the  $\text{CO}_2$  absorber, the flow may be continued at the original rate for 4 to 5 minutes, but in other trains, it may be desirable to reduce the flow of oxygen to about 150 ml per minute and so continue for 5 to 7 minutes after combustion. Close the oxygen valve, disconnect the  $\text{CO}_2$  absorber, and let it stand, preferably in the balance case, for 1 or 2 minutes, during which time the boat can be withdrawn from the furnace, the fusion inspected, and the boat placed under cover to cool for the next charge. Then, close the  $\text{CO}_2$  absorber and weigh it, using the counterpoise. If the fusion appears complete, deduct the light weight and multiply the difference by 10 to find the per cent carbon. If the smaller factor weight was used, multiply by 20, and if any other weight was employed, calculate the per cent carbon by the formula

$$\text{Per cent C} = \frac{\text{Weight of } \text{CO}_2 \times 0.2727 \times 100}{\text{Weight of sample}}$$

If the fusion appears incomplete, repeat the determination using a little more of the accelerator or a higher temperature.

In referee work, run two blanks before the combustion and pass the oxygen 3 minutes longer than normal. If the blanks agree closely, subtract their average weight from the weight of  $\text{CO}_2$  found before calculating the per cent carbon. If the blanks do not agree, repeat the runs until the blank is constant.

#### **Gravimetric Method: Weighing $\text{CO}_2$ as Barium Carbonate**

This method is used for the routine determination of carbon in several laboratories, and is satisfactory when time is not a factor. In districts where the humidity of the air is high, it has two advantages over methods that involve direct weighing of the carbon dioxide. It avoids the error due to the condensation of moisture upon the absorption bulb, and since the carbon conversion factor of barium carbonate is 0.0608 against 0.2727 for carbon dioxide, any error in weighing to decimilligrams is minimized. The apparatus and procedure are the same as described for the gravimetric method except that Meyer bulbs

filled with barium hydroxide are substituted for the ascarite or soda lime bulb and the flow of oxygen must be slower. Since the barium carbonate is weighed to find the carbon, it is obviously necessary to eliminate all sulphur oxides from the gases formed in the combustion before they enter the tube containing the barium hydroxide solution. This removal is effected by one of the approved methods already described. The Meyer tube, or bulb tube, is charged with the barium hydroxide by adding sufficient of the solution to the large bulb to fill most of the smaller ones, and after connection, the train is held in position by a suitable support.

### Procedure

Add the barium hydroxide to the bulbs and connect the latter as explained above. For pig or cast irons and other high-carbon alloys, use 10 times the factor weight, or 0.608 g of sample, for each combustion. For steels, increase this weight to 1.216 g for high-carbon steels and to 2.432 g or 3.04 g for low-carbon irons and steels. Spread the sample in a thin layer upon the lining of the boat and burn slowly. Allow about 30 minutes to burn the sample and flush all the  $\text{CO}_2$  out of the combustion tube.

Following the combustion and flushing period, disconnect the absorption tube from the combustion train, and perform the subsequent operations without delay to avoid contamination by  $\text{CO}_2$  from the air. Filter the barium hydroxide solution rapidly through a close filter paper by means of gentle suction. Wash the tube and paper immediately, 6 times with carbon dioxide-free water, using about 25 ml at each washing. Transfer the paper and precipitate to a weighed platinum crucible, heat gently until the paper is burned, and finally ignite at a temperature of  $850^\circ$  to  $900^\circ$  C. for 10 minutes. Weigh the crucible as soon as it has cooled, and subtract from this weight the tare and a proper allowance for blank to find the weight of barium carbonate. Multiply the weight of barium carbonate expressed in grams by 6.08 and divide this product by the weight of sample to find the per cent of carbon.

### Solutions and Blanks

#### Barium Hydroxide Solution

Barium Hydroxide ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ) .....	30 g
Water .....	1000 ml

The water is boiled and cooled rapidly, the barium hydroxide is added, and the solution is agitated occasionally until the hydroxide has dissolved. After any insoluble matter has settled, the clear solution is filtered into a container equipped with a guard tube filled with ascarite to exclude carbon dioxide from the air entering the vessel.

With ordinary care to see that the operations are carried through without delay, the blank due to filtering and washing without protec-

tion from the air is practically constant, and is determined by striking an average of several blank tests made at different periods during the day and continued for a number of days, or preferably at intervals over a period of several months.

### Volumetric Method for Titrating Excess Barium Hydroxide

Of the methods employing barium hydroxide as an absorbing agent, that depending upon absorption of the carbon dioxide in a measured amount of a saturated solution of barium hydroxide and titration of the excess is the one most widely used. Provision must be made in the combustion train for the removal of oxides of sulphur. To permit the use of a fixed volume of the barium hydrate, the weight of sample must be decreased for high-carbon and increased for low-carbon materials. For pig iron 0.5 g of sample is generally used, for steels 2 g.

### Procedure

Having observed the precautions mentioned above, weigh the sample carefully, spread it evenly upon the lining of the boat, and hold the latter in readiness to be inserted into the combustion tube. Transfer exactly 80 ml of the standard barium hydroxide solution, measured at the standard temperature, to the 500-ml absorption flask by means of an overflow pipette to avoid exposing the solution to the air. Immediately insert the rubber stopper carrying the bulb and inlet tubes into the flask, and connect the latter to the combustion train, the flask and bulb tube being inclined in such a position that the liquid in the flask will be forced into the bulb tube by the gas. Insert the boat into the combustion tube and turn on the oxygen gradually, adjusting it to give a rate of flow sufficient to provide an excess of oxygen during combustion of the sample. Note the appearance of the barium hydroxide solution which becomes slightly turbid in 3 to 7 minutes, indicating that oxidation of the sample has begun, and if necessary increase the flow of oxygen till the sample has burned, then reduce it to the normal rate. Continue the flow of oxygen 15 to 20 minutes longer, turn it off, and disconnect the absorption flask.

Hold the flask so that the bulb tube is in a vertical position, and as the barium hydroxide containing the precipitate of barium carbonate flows into the flask, rinse the bulbs with a stream of cold water free from carbon dioxide. When the precipitate has thus been washed into the flask, raise the stopper and wash the tip of the bulb as it is withdrawn from the flask. Add from 3 to 4 drops of phenolphthalein solution and titrate the excess barium hydroxide slowly with standard hydrochloric acid solution kept at the standard temperature, or at the same temperature at which the barium hydroxide was measured. During the addition of the acid, agitate the solution

in the flask and take the disappearance of the pink color as the end point.

From the acid equivalent of the barium hydroxide, as found from a blank determination carried out exactly as for an actual determination, subtract the volume required in the actual determination to find the acid equivalent to the barium carbonate formed during the combustion. Multiply this difference by the carbon value of the acid expressed in per cent to find the per cent carbon in the sample.

### Solutions Required

**Water.**—The water used for making the hydrochloric acid and barium hydroxide solutions, as well as that used for washing, must be free from carbon dioxide. The water is freed from this gas in two ways. The older method consisted in boiling the water for several minutes in a large flask, and cooling with the flask closed with a one-hole rubber stopper bearing a tube connected with a purifying bottle filled with sticks of sodium or potassium hydroxide, ascarite, or soda lime, or charged with a solution of sodium or potassium hydroxide, to remove carbon dioxide from the air in contact with the water.

A more recent method consists in bubbling filtered and purified air through the cold distilled water at a rapid rate for 15 to 20 minutes. Thereafter, the air may be bubbled through the water continuously at a slow rate, or the water may be kept in the bottle or flask closed with a guard tube as described above.

#### Standard Hydrochloric Acid Solution

Hydrochloric Acid (sp. gr. 1.19) .....	8 ml
Water free from carbon dioxide, to make .....	1000 ml

As a check on apparatus and reagents, also the technique of the analyst, this solution should be standardized theoretically through sodium hydroxide against acid potassium phthalate. One ml of 0.1 *N* HCl equals 0.0006 g carbon. However, it is ordinarily standardized by means of a standard steel. If this standard contains more than 0.50 per cent carbon, 1 g of sample is used, otherwise 2 g are employed. The sample of the standard is analyzed in exactly the same manner as a regular determination, and the percentage of carbon in the standard is divided by the number of ml of the acid equivalent to the barium carbonate formed to find the carbon value of 1 ml expressed in per cent. One milliliter of the solution above is equivalent approximately to 0.03 per cent carbon on a 2-g sample.

#### Standard Barium Hydroxide Solution

Barium Hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .....	20 g
Water free from carbon dioxide .....	1000 ml

The solution is made and allowed to assume room temperature, then filtered rapidly into a permanent container which has been filled with



filtered and chemically purified air. This container is fitted with a guard tube filled with ascarite or soda lime as an absorbent for carbon dioxide, and equipped with a siphon or other suitable connection to the measuring pipette or burette so that exactly 80 ml may be withdrawn without contact with the air. The temperature of this solution is kept the same as that of the standard hydrochloric acid.

#### Phenolphthalein Solution

Phenolphthalein .....	1 g
Alcohol (Neutral Ethyl) .....	1000 ml

The alcohol is best redistilled from quicklime and sodium hydroxide and diluted with CO<sub>2</sub>-free water. More concentrated or less concentrated solutions and a greater or smaller number of drops may be used, but as the end point is affected by the concentration of the reagent and the alcohol in the titrating solution, it is extremely important that exactly the same amount be used in each determination and in standardizing the solutions.

#### Text References

1. Hale, C. H., Jr., and Muehlberg, W. F., *Ind. Eng. Chem. (Anal. Ed.)*, **8**, 317 (1936).
2. "Ausgewählte Chemische Untersuchungsmethoden für die Stahl und Eisenindustrie," Otto Niezaldi.
3. Bower, J. H., *Natl. Bur. Standards J. Research*, **12**, February, 1934. Research paper 649, Sup't of Documents, Washington, D. C.

# Chemical Separations

## Introductory Remarks

Unlike carbon and a few other elements in steel, which can be rapidly separated from iron and the other elements present and obtained in a condition for direct determination in one process, many elements cannot be determined in the presence of iron and certain other elements and can be separated only along with certain others. To obtain these elements in a condition suitable for their determination, one or more preliminary separations may be necessary. Heretofore, it has been customary to describe these separations as a part of the method of determination. But since the same separation may be used for different elements, and different separations for the same element, simplicity and economy of space require that these separations be grouped and described separately. Hence, those separations that are or may be used in the determination of more than one element are described and their uses listed below, each being designated by the term commonly used in referring to it. Other separations are described in the procedures for the determination of the different elements.

## Bicarbonate Separation

### Elements Separated and Use of the Method

This method has long been advocated by the National Bureau of Standards. When carried out under the conditions of the procedure described below, it effects a separation as follows

The precipitate contains all of any Al, Cb, Ce, Cr, Ta, Ti, and Zr present and practically all of any  $\text{Fe}^{\text{III}}$ , P, V, U, Cu, and Sn present. By permitting a sufficient proportion of iron to be oxidized, all the phosphorus and vanadium may be precipitated.

The filtrate contains all the  $\text{Fe}^{\text{II}}$  and all but traces of Mn (0.005 per cent in steels containing less than 2.00 per cent Mn).

Elements that divide are cobalt, nickel, and tungsten.

The precipitate, therefore, may, by application of proper methods, be used for the quantitative determination of any of the first seven elements mentioned; the filtrate may be used for the routine determination of manganese by the persulphate method if cobalt is present and also by the bismuthate method if cobalt is absent. When exactness is necessary, the trace of manganese is recovered by treatment of the precipitate as described later.

Since cobalt divides, the separation cannot be applied, in the presence of this element, to the determination of manganese by the bismuthate method.

### Procedure

Transfer the desired weight of sample to a 300-ml Erlenmeyer flask, add 20 ml of dilute sulphuric acid (1:9) for 1 g of sample, plus 10 ml for each additional g, then cover and warm gently till the steel is dissolved. To remove insoluble matter, filter the solution rapidly and wash the filter thoroughly with hot water. Reserve the filter and, without delay, dilute the filtrate to about 200 ml with boiling water. Then add 35 ml of an 8-per cent solution of sodium bicarbonate (80 g  $\text{NaHCO}_3$  per liter) from a burette, shaking continually. Continue to add the bicarbonate solution more slowly until a slight precipitate forms, which is heralded by a change in color from a pea green to a yellowish green and an accelerated evolution of  $\text{CO}_2$ . Then, if chromium is under 5 per cent, add 4 ml in excess; if chromium is over 5 per cent, add 6 ml of the bicarbonate solution. Cover the container, add a little paper pulp, boil 1 minute, and filter as rapidly as possible as soon as the precipitate has settled. Wash the flask and precipitate 4 or 5 times with water containing about 1 g of sodium bicarbonate per liter. Reserve the filtrate and washings for the determination of manganese and the precipitate and the insoluble residue obtained from the first filtration for chromium, vanadium, etc., as required.

The precipitate and residue may contain a trace of manganese. Hence, if these insolubles are not to be used for a determination and extreme accuracy is desired, dissolve in aqua regia, fume with  $\text{H}_2\text{SO}_4$ , dilute, and precipitate Fe and Mn by adding  $\text{Na}_2\text{O}_2$ . To recover the manganese, boil, filter, and redissolve with dilute  $\text{HNO}_3$  (1:1) containing a little  $\text{NaNO}_2$  or  $\text{SO}_2$ . Add the solution to the filtrate or oxidize with persulphate or periodate and estimate the manganese by color. The latter treatment permits a recombination of the two portions representing the bicarbonate precipitate, if care is observed to use a minimum of reagents for the recovery.

### Zinc Oxide Separation

#### Elements Separated and Use of the Method

In this separation, provided only one separation is made, the iron and chromium, if both are in the trivalent state, are obtained in the precipitate. Ferrous iron remains largely in solution and tungsten goes with the iron if it is oxidized as in the procedure below; otherwise it divides. Separations, therefore, are affected by the state of oxidation or reduction of the solution and by the presence or absence of certain other elements.

A. In reduced acid solution, such as is obtained by dissolving steel in sulphuric or hydrochloric acid:

The precipitate contains all or practically all of any Al, Cb, Cr, Cu, Mo, Ta, Ti, V, and Zr present.

The filtrate contains all or practically all of the Fe, Mn and Ni, and Co, if Cu and Mo are absent.

Elements that divide are W and Co, if Cu or Mo is present.

B. In acid solution oxidized with nitric acid:

The precipitate contains all or practically all of the Al, Cb, Cr, Cu, Fe, Mo, P, Ta, Ti, V, W, and Zr.

The filtrate contains all or practically all of the Mn and Ni and Co, if Cu and Mo are absent.

Cobalt divides if Cu or Mo or both are present.

C. In a perchloric acid solution which has been fumed strongly: Chromium may remain largely in solution with the manganese, nickel, and cobalt; and some of the manganese is always oxidized. However, this objection to perchloric acid is readily overcome by diluting 100 per cent or more and adding a freshly prepared saturated solution of sulphur dioxide or a 5- to 10-per cent solution of sodium sulphite.

The separation, therefore, is used mainly in the determination of manganese; and since it is difficult to wash the voluminous precipitate from an oxidized solution free of manganese, or compensate for the volume it occupies, if the solution for analysis is obtained by decantation, precipitation in reduced solution is preferable. In addition, precipitation in reduced solution gives a solution with most of the iron present, and similar to a plain-carbon steel with the same percentage of manganese, thus permitting the use of the same standards.

### Procedure

Transfer two times the weight of sample desired for the determination to a 500 ml Erlenmeyer flask, add 25 ml of dilute perchloric acid (10 ml 60-per cent + 15 ml  $H_2O$ ) or 25 ml dilute sulphuric acid (1:4), and heat gently until the steel has dissolved.

Instead of either of these acids, hydrochloric acid may be used, and a mixture of hydrochloric and nitric acids may be used for high-alloy steels.

If tungsten is present and the steel was dissolved in hydrochloric or sulphuric acid, add slowly 5 ml of nitric acid and boil to the disappearance of red fumes. If hydrochloric acid is used alone or in combination with other acids, and the solution is to be used for the determination of manganese, evaporate it and fume strongly with sulphuric or perchloric acid. Cool, add 100 ml of cold water, and if the solution was fumed with perchloric acid, add 10 ml of a saturated solution of  $SO_2$  to reduce chromium and manganese compounds.

Add ammonia in small quantities while shaking vigorously until a slight precipitate that barely dissolves is formed. Transfer the solution to a 200-ml volumetric flask and rinse the Erlenmeyer flask with cold water. To precipitate iron, etc., add zinc oxide emulsion (prepared as described below) in portions of about 5 ml each, shaking after each addition until the color of the solution resembles that of coffee and cream, and a further addition causes the precipitate to appear lighter in color. Dilute to the mark, mix well, and allow the precipitate to settle a few minutes.

Filter the solution through a dry filter, discarding the first 10 to 15 ml and collecting the remainder in a clean, dry beaker. With a pipette calibrated against the flask, transfer 100 ml to a suitable container to give a portion representing the sample desired for analysis.

The precipitate may retain a trace of manganese, particularly if the solution was not reduced with  $\text{SO}_2$ . Hence, some prefer to start with no more sample than is required for manganese and use all the filtrate from the insoluble matter, redissolving and examining the latter for manganese. However, any loss of manganese held by the precipitate is partly, if not wholly, compensated for by the fact that the solution is somewhat too concentrated, due to the volume occupied by the precipitate.

**Zinc Oxide Emulsion.**—Mix water gradually with pure finely powdered zinc oxide, first rubbing to a paste in a mortar, until the mixture has the consistency of cream.

### Lead Perchlorate Separation of Chromium in Presence of Manganese, Titanium, Vanadium, and Aluminum.

#### Uses of the Method

This method is convenient when it is necessary to separate only the larger part of the chromium, and the introduction of lead is not objectionable, as in the determination of manganese and titanium in stainless steels. Chromium may not be completely precipitated, but the small portion that sometimes remains in solution does not affect some determinations. The solubility of lead chromate depends upon the percentage of  $\text{HClO}_4$  and lead perchlorate in solution. It is completely insoluble in 1 *M*  $\text{HClO}_4$  with 0.01 *M* lead perchlorate, and practically insoluble in 5 *M* acid if twice as much lead is present. The  $\text{HClO}_4$  required to combine with 1 g of iron is 5.6 ml of 70-per cent grade. Therefore, in calculating percentage of free acid, 7 ml of 55-per cent acid or 6 ml of 60-per cent acid per gram of steel should be subtracted from the amount used.

One ml of 55-per cent acid contains 0.81 g  $\text{HClO}_4$  and the concentration is 8 *M*.

One ml of 60-per cent acid contains 0.92 g  $\text{HClO}_4$  and the concentration is 9 *M*.

These data permit calculation of the proportion of acid used and of the dilution desired.

### Special Solutions Required

**Lead Perchlorate Solution (0.5 Molar).**—Lead perchlorate,  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ , suitable for this solution may be purchased. With it a half-molar solution is made by dissolving 1 pound of the salt in water and diluting to 1970 ml.

As the salt is expensive, some chemists prefer to prepare the solution from lead nitrate. The procedure is as follows:

Place 166 g of pure lead nitrate  $\text{Pb}(\text{NO}_3)_2$  in a casserole with 110 ml of 70- to 72-per cent C. P. perchloric acid and 50 ml of water, adding the water first. To dissolve the nitrate, place the dish on a sand bath and evaporate to fumes of perchloric acid, during which operation the nitrate will dissolve. Rinse down any salt on the wall of the casserole with 30 ml of water and repeat the evaporation, keeping the temperature below  $100^\circ \text{C}$ ., at which temperature lead perchlorate decomposes. Test the solution for nitric acid by dropping a drop into a strong sulphuric acid solution of diphenylamine on a spot plate. If a blue color develops, add 30 ml of water again and evaporate the solution, repeating these operations until the test for nitric acid is negative. After cooling, dilute the contents of the dish to about 800 ml, filter the solution, discard any insoluble matter, and dilute to 1 liter with distilled water.

**Silver Perchlorate Solution (0.5 Molar).**—This salt can be purchased in the market or prepared as follows:

To prepare 100 ml, treat 8.5 g of silver nitrate as in the preparation of the lead perchlorate, using one-tenth of the quantity of reagents throughout.

### Procedure

Transfer the required weight of sample to a 125-ml Erlenmeyer flask (or to a beaker for the larger samples), add 12 ml of 55-per cent perchloric acid for 0.5 g of sample, 20 ml for 1.0 g or 35 ml for 2 g, and apply gentle heat until the steel has dissolved.

Steels that dissolve very slowly with the dilute perchloric acid may be dissolved with hydrochloric and nitric acids, but a little more perchloric must then be added, and the mixture boiled down and fumed until all traces of the dissolving acids have been expelled.

When the steel is in solution, increase the temperature to boiling and continue till the chromium begins to oxidize. At this point cover the mouth of the flask and boil gently till the inside of the flask is clear of fumes, and for 3 minutes thereafter. Finally, boil vigorously for a few seconds, cool in air about 10 seconds, rotating the flask, and complete the cooling in water. As soon as the liquid has solidified, add water equal to twice the volume of 55-per cent  $\text{HClO}_4$ .

used, stir until the salts have dissolved, and boil 1 minute. Remove from the heat and add a few drops of the silver perchlorate solution to precipitate any chlorine present. Now, add sufficient lead perchlorate to precipitate the chromium—4 ml for each 100 mg of chromium, plus an excess equivalent to 4 per cent of the volume—stir, and immediately cool in water. When cool, filter the solution into another Erlenmeyer flask, wash the original flask, the filter, and precipitate with a small amount of water. Reserve the solution for the determination of manganese, titanium, vanadium, or aluminum.

### **Perchloric Acid-Ammonium Persulphate Separation for Manganese**

#### **Elements Separated and Use of the Method**

This method depends upon the oxidation of the chromium with perchloric acid, following which operation the manganese is precipitated along with the iron and other elements with ammonia and ammonium persulphate, under the conditions of precipitation as described in the procedure below.

The precipitate may be expected to contain all the As, Fe, P, V, Ti, Sn, Si, Zr, U, Cb, and Ta and practically all the manganese.

The filtrate contains all or nearly all the Cr and W.

Elements that divide are Al, Cu, Co, and Ni.

The separation is used mainly for the determination of manganese.

#### **Procedure**

Transfer the sample to a 400-ml beaker and dissolve in perchloric acid (C.P. dilute) a mixture of equal parts of hydrochloric and nitric acids, or in hydrochloric acid followed by nitric acid, using as small a volume of the acids as practicable. If the mixed acids are used, add 20 ml of perchloric acid (70- to 72-per cent) as soon as the steel has dissolved. Boil the solution until it reaches the fuming stage, cover the beaker, and fume strongly for 10 minutes after the solution changes color, usually from brown to red or orange. Cool for a few seconds in air, then in running water, add 2 or 3 volumes of water, and boil. Dilute to about 200 ml with hot water, stir and add ammonia till a slight precipitate forms, then add 2 or 3 g of ammonium persulphate and 15 ml of ammonia, and heat rapidly to boiling. After boiling 5 minutes, add a little more persulphate and about 5 ml of ammonia, and permit the precipitate to settle. Filter rapidly, wash 3 or 4 times with hot water containing a little ammonia and ammonium persulphate, and dissolve the precipitate into the original beaker with 20 to 30 ml of warm dilute sulphuric acid (1:4) saturated with  $\text{SO}_2$ . Wash the filter with water, evaporate the filtrate and washings to the fuming stage, rinse the wall of the beaker with a fine jet of water, evaporate, and fume 5 to 10 minutes to

eliminate all traces of chlorides which may have been collected in previous operations. Finally, dilute to 100 ml with water and reserve for the determination of manganese by either the persulphate or bis-muthate methods, adding 6 ml of nitric acid and 3 ml of phosphoric acid (85-per cent) if the former method is to be employed.

### Chlorate Method for Isolation of Manganese

This method has been used mainly for the separation of manganese preliminary to its determination gravimetrically or volumetrically. Objections to the method are:

1. Precipitation of the manganese is not quite complete, particularly if it is present in small proportions ( $<1$  mg) or if molybdenum and antimony are present, when results will be 0.01 to 0.03 per cent low.

2. The precipitate is likely to carry down with it traces of iron, chromium, cobalt, and vanadium.

3. The oxidation gives off a great deal of acid fume somewhat irritating to the mucus membranes.

If the method is employed to eliminate large amounts of manganese which might interfere with the determination of some other element, the first objection does not apply; for the determination of manganese by the persulphate method, the second can be ignored; and the third is overcome by performing the operation in a good hood.

### Procedure

Transfer the required weight of sample (0.5, 1, or 2 g) to a 400-ml tall form beaker, and add 10 ml of water and 10 ml of perchloric acid (70-72 per cent). If this acid fails to act on the steel, add 15 ml of hydrochloric acid and 5 ml of nitric acid. When the steel is in solution, add 5 ml more of the perchloric acid.

Alternately, the sample may be dissolved with a mixture of hydrochloric and nitric acids and 15 ml of the perchloric acid added after solution is complete. If tungsten is present, as indicated by a yellow residue, dilute and filter before adding the perchloric acid. Boil uncovered until fumes appear, then rinse the wall of the beaker with a fine jet of hot water, cover, and apply heat till the beaker is clear of fumes and perchloric acid is condensing freely upon the cover and upper wall of the beaker, or until salts begin to separate, if 2 g of sample were used. Cool somewhat, add 50 ml nitric acid (sp. gr. 1.42), and heat to boiling. Remove the beaker from the source of heat, pull the cover to one side, add a few crystals of sodium chlorate ( $\text{KClO}_3$  cannot be used because of the low solubility of  $\text{KClO}_4$ ), and when the foaming ceases, add 2 g cautiously. Heat to gentle boiling for 5 minutes and again add 2 g of the sodium chlorate as before. Simmer for 5 minutes, avoiding overheating, which decomposes the chlorate too rapidly, add 2 g of the salt, and



simmer again for 5 minutes. Finally, add 2 g of the sodium chlorate and filter rapidly through a close, thin, filter pad of purified asbestos which has been prepared as described below and has just previously been washed with hot colorless nitric acid. To prepare this acid, boil it for 5 minutes and keep it at the boiling point until used. Rinse the beaker with a few ml of the colorless nitric acid, and add the acid to the funnel just as the filter goes dry. Repeat the washing with the acid till the washings are colorless. If manganese is to be determined volumetrically, wash the beaker and the filter free of chlorides (3 to 4 times usually) with cold water. If manganese is to be determined gravimetrically, omit the washing with water as it tends to dissolve the  $\text{MnO}_2$ .

Discard the filtrate and washings, replace the receiving vessel with a clean one, and dissolve the  $\text{MnO}_2$  by washing the beaker and the filter with 50 ml of a 5-per cent solution of nitric acid to which 10 ml of 3-per cent hydrogen peroxide has been added. Wash the beaker and filter 2 or 3 times with water, boil the solution to decompose the peroxide, and reserve for the determination of manganese by the method selected.

**Asbestos Filter.**—Shred long fiber asbestos, ignite gently, digest several hours with  $\text{HCl}$ , wash with water on a ribbed funnel with a platinum cone, digest 5 hours with 3 per cent solution of  $\text{HNO}_3$ , wash as before and mix with water. To make a filter, use a carbon filter tube with perforated porcelain disc, just cover the disc with fine-fiber glass wool, add enough of the asbestos suspension to form a thin tight filter, apply suction, wash thoroughly with water, and finally treat as best suited to the purpose for which it is to be used.

### Ether Separation

#### Use of the Method and Elements Separated

This separation, frequently referred to as the "ether extraction method," has long been used as a means of removing most of the iron from a solution preliminary to the determination of other elements. Briefly, it consists in mixing a cold oxidized chloride solution with ether, allowing the two liquids to separate, and drawing off the heavier acid solution from the lighter ether layer. In the analysis of steels, it is much used in the determination of sulphur, and of small percentages of elements such as Al, Cr, Co, Ni, Ti, and Zr in carbon steels, and of Mn in ingot irons. Where properly applied as an initial step in the analysis of steel, molybdenum is the only element completely extracted from others, the results of a single extraction being as follows:

The one element wholly extracted and found in the ether layer is molybdenum.

Elements partly extracted are:

Element	As <sup>III</sup>	As <sup>V</sup>	Cu	Ga	Ge	Au <sup>III</sup>	In	Ir <sup>IV</sup>	Fe <sup>III</sup>	Hg
Per Cent in Ether	68	4	trace	97	50	95	trace	5	99	0.02
Element	P	Pt	Se	Tl		<sup>III</sup> Sb <sup>V</sup>	Sn <sup>II</sup>	Sn <sup>IV</sup>	V	Zn
Per Cent in Ether	12-27	trace	trace	95		81	30	17	trace	0.2

Elements wholly left in the acid solution are: Al, Ag, Bi, Ca, Cd, Cr, Co, Gl, Fe<sup>II</sup>, Pb, Mn, Ni, Os, Pd, Rh, S, Th, Ti, W, U, Zr.

Practically complete separation of some of the elements partly extracted can be had by repeating the treatment one or more times.

### Procedure

The optimum conditions for an extraction are:

1. All elements must be present as chlorides in cold medium-concentrated hydrochloric acid solution (sp. gr. 1.10) with the iron in the trivalent (oxidized) state.

2. The concentration of iron should not exceed 1.0 g for each 10 ml of solution when sharp separations of this element are desired.

3. For each 20 ml of solution not less than 30 ml of ether should be used, but usually a satisfactory separation may be had by using 200 to 250 ml of ether with 10 g of Fe in 50 ml of acid solution.

4. The ether used must be reasonably free of alcohol.

In the analysis of steel for small proportions of elements, samples as large as practicable are desirable. Tested treatments of samples for small proportions of elements, such as in the determination of low percentages of chromium, are as follows:

**For a Sample of 5 g.**—Weigh and transfer the sample to a 400-ml beaker. Add 60 ml of hydrochloric acid (sp. gr. 1.13), heat gently till the metal has dissolved, and oxidize the solution by adding concentrated nitric acid dropwise and cautiously until there is a final "puff" or effervescence, indicating that all the iron has been oxidized to the ferric condition.

Evaporate the solution to dryness, cool slightly, and add 25 ml of hydrochloric acid (sp. gr. 1.19). Stir and heat gently to dissolve the residue, but do not boil. Cool the solution to 20° C. or lower and transfer it to a 400-ml separatory funnel, using dilute hydrochloric acid (sp. gr. 1.13) for rinsing.

Following the directions given above as the optimum conditions, some chemists dissolve the residue from the evaporation and dilute to 100 ml with dilute hydrochloric acid having a specific gravity of 1.10. In other hands the procedure as given above has been found to give satisfactory results.

Add 250 ml of pure ethyl ether to the funnel, stopper the funnel, and shake under a stream of cold running water if necessary to keep the solution cool. Clamp the separatory funnel in a vertical position

until the two liquids separate into distinct layers, then draw off the lower acid layer containing but little of the iron into a 200-ml Erlenmeyer flask until the ether layer approaches the stopcock. Turn the stopcock barely enough to close off the stream, wash the neck of the flask with HCl, and allow the mixture to stand 5 minutes. Then, carefully draw off the rest of the acid layer completely. In exact work wash the ether with HCl (sp. gr. 1.10) saturated with ether. Evaporate the acid solution in the flask to 25 ml or less to drive off the dissolved ether. Then, to destroy organic matter completely, add  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , and evaporate to fumes.

**For a Sample of 10 g.**—Dissolve the sample with 70 ml of hydrochloric acid (sp. gr. 1.13) and oxidize the iron by adding nitric acid,  $\text{HNO}_3$  (sp. gr. 1.42), dropwise. Evaporate to a syrupy consistency. Cool and add 30 ml of hydrochloric acid (sp. gr. 1.19).

Transfer the cold solution to a separatory funnel, using dilute HCl (sp. gr. 1.13) for rinsing. Add 350 ml of pure ethyl ether, shake thoroughly, and complete the separation as directed for a sample of 5 g.

**For a Sample of 2 g.**—Weigh and transfer the sample to a 250-ml flask. Add 30 ml of hydrochloric acid (sp. gr. 1.13), and when the cuttings have dissolved, add nitric acid (sp. gr. 1.42), dropwise and cautiously, to avoid an excess until the iron is just oxidized as indicated by a slight effervescence. Boil the solution clear of fumes, cool, and add 10 ml of hydrochloric acid (sp. gr. 1.19). Transfer the cold solution to a separatory funnel, using dilute hydrochloric acid (sp. gr. 1.13) for rinsing, add 70 ml of pure ethyl ether, shake well, and complete the separation as directed for a 5-gram sample.

### Separation with Cupferron

In the past this organic salt (ammonium nitrosophenylhydroxylamine,  $\text{C}_6\text{H}_5\text{N} \cdot \text{NO} \cdot \text{ONH}_4$ ) has been used more in the analysis of rocks, refractories, and similar substances than in the analysis of steels. The elements precipitated vary with conditions, whether alkaline, neutral, weakly acid, strongly acid, reduced, oxidized, hot, or cold. As ferric iron is completely precipitated along with the other elements generally sought, precipitations in the analysis of steels are usually made in strongly acid reduced solutions, when most of the iron remains in solution. Under the conditions of the procedure given below, the separations are about as follows:

**Elements Completely Precipitated.**—Cb, Cu(?),  $\text{Fe}^{\text{III}}$ , Ga, Sn, Ta, Ti,  $\text{U}^{\text{IV}}$ , V, Zr.

**Elements Partly Precipitated.**—Cu,  $\text{Fe}^{\text{II}}$ , Si, Th, W.

**Note:** Ba, Ce, Hg, Pb,  $\text{Sb}^{\text{III}}$ , Ag, the rare earths, if present or added, also large percentages of phosphorus, alkalis and alkaline earths, will contaminate the precipitate.

Complete precipitation of copper occurs only in solutions that are but slightly acid.

**Elements that Remain in Solution.**—Al, As, Be, Cr, Mn, Mo, Ni, P, Sb<sup>v</sup>, U<sup>vi</sup>, Zn.

### Special Reagent Solution

A 6-per cent water solution of cupferron is used. The solution is not stable and should be made up daily, or as used, and kept cold. The reagent, itself, must be prepared with care and kept in a cool, dark place to prevent some decomposition. A small bag of ammonium carbonate suspended from the stopper of the container also helps preserve the reagent.

### Procedure

Dissolve 2 g to 10 g of the sample, according to the amount of the element sought that may be present (10 g always for carbon steels) in 150 to 250 ml of dilute sulphuric acid (5- to 8-per cent) contained in a 400-ml beaker. Cover and heat to 90 to 95° C to hasten solution. Cool the solution to 15° C or below, and, while stirring constantly, add the cold cupferron solution dropwise until the precipitate assumes a reddish brown color. The addition of the cupferron beyond this point causes more iron to be precipitated and serves no useful purpose. Filter the solution through an 11-cm paper, using paper pulp, and wash 10 to 12 times with cold dilute sulphuric acid (1-per cent), preferably containing also 1 per cent cupferron. Discard the filtrate. Transfer the paper and precipitate to the beaker in which the precipitation was made and oxidize organic matter by digesting with 20 ml of nitric acid and 10 ml of sulphuric acid, adding nitric acid as required and evaporating to fumes one or more times.

If precaution is taken to add the nitric acid first (25 to 40 ml), 15 to 20 ml of perchloric acid (55- to 60-per cent) may be substituted for the sulphuric acid, if the perchloric acid is added slowly and cautiously, when one evaporation to fumes may be sufficient to destroy all the carbonaceous matter.

When the paper and organic matter have all been consumed, cool, dilute, and treat the solution according to the element to be determined as follows:

For vanadium, dilute to 300 ml, add 3 ml of H<sub>3</sub>PO<sub>4</sub> (85-per cent), stir in a dilute solution of KMnO<sub>4</sub> till the color is pink, reduce, and titrate as directed under vanadium.

For titanium or titanium and vanadium, dilute and proceed as described under titanium.

For columbium, tin, tantalum, or zirconium, dilute, pass H<sub>2</sub>S to separate copper (only if fumed with H<sub>2</sub>SO<sub>4</sub>), filter, and treat the filtrate as may be necessary to separate the element desired.

## Separation of Chromium as Chromyl Chloride

### Principles and Application of the Method

This novel method for the selective separation of chromium involves volatilization of the element from a perchloric acid solution of the steel as chromyl chloride, which is formed by the addition of sodium chloride or concentrated hydrochloric acid to the fuming acid solution. The method is extremely rapid, and that it provides an efficient means for eliminating chromium is indicated by the fact that the chromium content of a solution of a 1-g sample of 27-per cent chromium steel is reduced to 0.15 and 0.40 per cent in 5 to 10 minutes, including the time required to dissolve the sample. Also, through proper technique, all the chromium may be eliminated. Finally, the phenomenon is of interest as explaining the low results for chromium occasionally obtained in methods involving oxidation of this element with perchloric acid.

The method was first applied\* to facilitate the determination of manganese in high-chromium steels, then to the determination of vanadium. Also, as explained at the end of this section, it may be applied to other determinations in which large proportions of chromium interfere; its advantages in the determination of manganese become apparent when it is compared with the usual zinc oxide method for separating chromium in the analysis of stainless steels for manganese. To quote the originator of the method:

"In the zinc oxide method, the solution in 9-N  $\text{H}_2\text{SO}_4$  may require from  $\frac{1}{2}$  to 2 hours, and the filtration of the  $\text{ZnO}$  precipitate is very slow, especially if the solution is oxidized and ferric hydroxide is present. The use of perchloric acid for the solution of the steel makes solution possible in 5 to 10 minutes. If oxidation is postponed until after the separation of chromium, the filtration is much faster, but in attempting to combine these two improvements it was practically impossible to keep the iron in the ferrous state in perchloric acid solution.

"The old method of distinguishing between chlorides and bromides by means of the gases evolved by heating the solid halide with potassium dichromate and concentrated  $\text{H}_2\text{SO}_4$  offered a possible solution. Therefore, experiments were begun with the object of determining if chromium could be removed by volatilization as  $\text{CrO}_2\text{Cl}_2$  sufficiently so that manganese could be determined in the solution remaining. An early experiment showed that  $\text{H}_2\text{SO}_4$  was not necessary for the evolution of chromyl chloride. Further experiments with perchloric acid solutions led to the following procedure, which has proved eminently satisfactory as a preliminary step in the analysis of many types of stainless steels by the standard persulphate arsenite method."

\* Unpublished report by Fred Wilson Smith, February 12, 1937, South Works Chemical Laboratory, Carnegie-Illinois Steel Corporation, Chicago, Illinois.

### Procedure for Solution of the Sample and Elimination of Most of the Chromium

To 1 g of sample in a 500-ml Erlenmeyer flask, add 25 ml of a mixture composed of 1 part dilute HCl (1:1) and four parts HClO<sub>4</sub> (72-per cent). Place the flask on a hot plate, and as soon as solution is complete, fume as usual until the chromium is oxidized. Now, to eliminate the chromium, add 1 to 2 g of NaCl in small portions and continue until the chromium has been reduced to the percentage desired, or until no noticeable fumes of CrO<sub>2</sub>Cl<sub>2</sub> are evolved. This procedure should reduce the chromium content of the solution to between 0.15 and 0.40 per cent.

If it is desired to avoid the high salt concentration produced by the use of NaCl, concentrated hydrochloric acid may be substituted. In the use of HCl, the fuming solution is cooled slightly, 1 to 2 ml of HCl is added while the flask is being swirled, and heat is again applied to the flask until the HClO<sub>4</sub> is fuming, and the chromium is completely oxidized. These operations are repeated until all the chromium has been expelled.

### Procedure for Eliminating All the Chromium

To eliminate all the chromium, the amounts of perchloric acid and of sodium chloride used are varied according to the weight of sample and the per cent chromium in the steel. For a 2-g sample containing 18 to 30 per cent chromium, the procedure is as follows:

Transfer the weighed sample to a 500-ml Erlenmeyer flask and add 10 ml of HCl and 50 ml of HClO<sub>4</sub> (60-per cent). Cover the flask and heat to about 90° C until the sample dissolves, then increase the temperature to evaporate the H<sub>2</sub>O and HCl rapidly and completely oxidize the chromium, fuming for at least 5 minutes after the last change in color to make sure the oxidation is complete. Remove the cover from the flask and add dry NaCl a little at a time, swirling the liquid in the flask after each addition of the salt, until the brown fumes of chromium oxychloride are no longer given off. After 3 or 4 more additions of the sodium chloride, cool the flask and contents somewhat, and with a fine jet of water, rinse the wall of the flask clean of adhering chloride. Add 10 ml of HClO<sub>4</sub>, cover the flask, and repeat the fuming with sodium chloride additions as before; and if the chromium is above 20 per cent, rinse the wall of the flask a second time, fume and treat again with NaCl, adding in all about 10 g of the salt. When the last of the NaCl has been added, continue the heating with the flask covered until the condensing perchloric acid has rinsed down all the NaCl adhering to the wall of the flask and until all the HCl has been dispelled, if it is necessary to have the solution free of chlorides.

The method requires practice to insure complete volatilization of the chromium; and, until the analyst becomes proficient, the solution

should be tested for chromium when it is necessary to eliminate the last traces of this element.

### Effect of the Treatment upon Other Elements

Following the experiments leading to the methods outlined above, other investigations were conducted to ascertain the effect of the treatment upon 20 other elements that may be present in steel. These experiments indicated that,

**Tin** is partly or wholly volatilized, depending upon conditions, the tin being expelled during the fuming through the reactions of the sodium chloride.

**Arsenic** is not volatilized to the extent that might be expected, though analysis of the solution remaining after the treatment by some volumetric and gravimetric direct methods indicates losses varying from 10 per cent to 95 per cent of the total arsenic present. Application of the distillation method showed losses of 2 to 4 per cent of the arsenic. Apparently it is extremely difficult to reduce all the arsenic in the presence of perchloric acid.

### Loss of Other Elements and Interference of Perchloric Acid

Experiments indicate that, while the treatment leaves a solution of perchloric acid which may interfere with the determination of many elements by certain methods, fuming with either  $\text{HClO}_4$  or  $\text{HClO}_4$  and  $\text{NaCl}$  results in no appreciable loss of Al, B, Be, Cb, Co, Cu, Fe, Mo, Ni, P, S, Sc, Ti, U, V, W, Zn or Zr.

The same experiments show that the perchlorates or free perchloric acid that remains in the solution following the treatment interferes in the determination of titanium, selenium, aluminum, and tungsten in the following ways.

1. The solution prevents the complete precipitation of titanium by cupferron and sodium thiosulphate, and unless certain other elements that may be present are removed, the titanium cannot be determined by color. In the absence of other interfering elements, chromium may be removed and titanium subsequently determined by color. Also, provided iron is absent or present in limited small proportions, titanium may be completely precipitated with sodium thiosulphate.

2. In the determination of aluminum, the solution from the treatment interferes in the separation of this element by either the phosphate or the thiosulphate methods, but does not prevent its complete precipitation with ammonia.

3. Low results for tungsten are obtained on solutions of steels treated initially by this method for the elimination of chromium. This apparent loss, however, is not due to the treatment or to the presence of either perchloric acid or perchlorates. After oxidizing

W to  $\text{WO}_3$  with  $\text{HNO}_3$ , adding cinchonine, and filtering, the precipitation of tungsten continues slowly in the filtrate. One explanation for the phenomenon observed is that no phosphorus is lost, as may be the case when the initial solution is effected with  $\text{HCl}$ , so that conditions promote the formation of the phosphotungstate, which delays the precipitation.



# Determination of Manganese

## Methods and Their Application

While manganese may be determined gravimetrically, it is almost universally determined in steel volumetrically by one of two methods, known as the persulphate and the bismuthate methods, which terms refer to the reagents used in oxidizing the manganese in solution. The bismuthate method may be used for the direct determination of manganese in all steels except those containing cobalt, to which steels it is not applicable by any modification that does not involve a separation of the two elements. In the presence of cobalt, manganese is most expediently determined by the persulphate method. Neither method is applicable without modification to steels containing tungsten or more than 3.0 per cent chromium, and most analysts prefer to separate this element when it exceeds 1 per cent for the persulphate method or 0.5 per cent for the bismuthate method. Both methods have limitations as to the percentage of manganese that can be titrated visually, but by varying the weight of sample taken, the highest percentages found in steels, including the 12- to 14-per cent manganese steels, can be accurately determined. By titrating potentiometrically, larger proportions of manganese may be determined.

**Caution.**—In both methods, extreme care is required to avoid contamination of the solution with chloride ion in any form prior to oxidation of the manganese. Following oxidation of the manganese, neutral chlorides reduce the permanganic acid slowly in cold solution, and hydrochloric acid much more rapidly.

## THE PERSULPHATE METHOD

This method involves oxidation with ammonium persulphate and silver nitrate, and titration of the permanganic acid with sodium arsenite.

## Weight of Sample

For visual titrations, the weight of sample should be varied according to the proportion of manganese present, about as follows:

Per Cent Manganese Present	Weight of Sample
Under 0.05	1.0 g or 2.00 g
0.05 to 1.00 or 1.50	0.5 g or 1.00 g
1.00 to 2.00	0.50 g
1.50 to 2.00	0.25 g to 0.50 g
2.00 to 5.00	0.10 g to 0.25 g

More than twice these amounts may be used if the titration is made potentiometrically.

### Applications of the Method to Plain-Carbon and Low-Alloy Steels

By rigidly fixing the conditions, several modifications of this method have been successfully used for manganese in carbon steels. Now, for plain-carbon steels and low-alloy steels containing less than 1 per cent of tungsten or chromium, two modifications are in use, both of which have been proved accurate and most satisfactory for the routine determination of this element. Experiments have shown that nickel may be present in any proportions and that titanium up to 5 per cent is without effect upon the results. Procedures for the two modifications are given as follows, Procedure II being preferred by most analysts.

### Procedure I—Visual Titration with Precipitation of Silver Ion

**Absence of Chromium or Tungsten.**—Dissolve 0.5 g in 10 ml of dilute nitric acid (sp. gr. 1.20) in a 150-ml Erlenmeyer flask. Add 5 ml of 15-per cent ammonium persulphate solution and boil—not too long else a trace of  $\text{MnO}_2$  may be formed if the acidity is low. Add silver nitrate-sulphuric acid solution and 15-per cent ammonium persulphate according to the manganese present as shown in the following table:

Per cent Mn	$\text{AgNO}_3\text{-H}_2\text{SO}_4$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	NaCl solution
0.0 -1.60	15	10	5
1.60-2.60	20	20	8
2.60-3.00	25	20	10
3.00-4.00	30	20	12

The  $\text{AgNO}_3\text{-H}_2\text{SO}_4$  mixture contains 5 g  $\text{AgNO}_3$  and 250 ml of 1:1  $\text{H}_2\text{SO}_4$  per liter. The NaCl solution contains 5 g pure NaCl per liter.

Heat to  $85^\circ\text{C}$  until the color is fully developed and a foam appears on the surface. Cool to  $25^\circ\text{C}$ , add NaCl solution in amount as shown in the table, and titrate rapidly with  $\text{Na}_2\text{HAsO}_3$  solution standardized against a standard steel, or reduced  $\text{KMnO}_4$ , in which Mn is oxidized in the same way as the determination is made. If the titration is made slowly, results may be low, due to reduction of the permanganic acid by the chloride.

**Presence of Chromium or Tungsten.**—*Chromium Under Five Per Cent.*—Weigh and transfer the sample to a 150-ml Erlenmeyer flask, add 25 ml of water, 5 ml of dilute sulphuric acid (1:1), and heat gently until all effervescence ceases, adding 3 ml of orthophosphoric acid (85-per cent) if tungsten is present. Add 10 ml of dilute nitric acid (sp. gr. 1.20) and boil to a clear solution. Add from 15 to 40 ml of a 0.5-per cent solution of silver nitrate and 10 to 20 ml of the ammonium persulphate according to the manganese and chromium present, the larger volumes being required for 4-per cent chromium

tungsten steel. Complete the determination as described above for manganese in the absence of tungsten and chromium, titrating rapidly and immediately after adding the sodium chloride.

*Chromium Over Five Per Cent.*—Dissolve the sample and separate the chromium by the lead perchlorate, sodium bicarbonate, or zinc oxide separations, but preferably by volatilizing it as given in the last method under *Separations*; and proceed as outlined above. For example: Following the lead perchlorate separation, after filtering to separate the lead chromate, add to the filtrate 10 ml of dilute nitric acid (sp. gr. 1.20), boil, add silver nitrate-sulphuric acid solution, oxidize with ammonium persulphate solution, and complete the determination, all as directed above.

### Procedure II: Visual Titration in Presence of Silver Ion

Weigh and transfer the sample (see under *Weight of Sample*, page 74) to a 400-ml beaker or a 500-ml Erlenmeyer flask. Add 25 to 30 ml of the nitric-sulphuric-phosphoric acid mixture and heat gently. If solution is slow, add 2 to 5 ml water. If much nickel or chromium is present, solution may be hastened by adding 5 ml of dilute  $H_2SO_4$  (1:1), heating gently until solution is almost complete, and then adding 7 ml of nitric acid and 3 ml of orthophosphoric acid (85-per cent).

Boil the solution till oxides of nitrogen are expelled and dilute with 100 ml of water, preferably hot to save time. Add in succession 5 ml of a 1-per cent solution of silver nitrate and 10 ml of a 30-per cent solution of ammonium persulphate. Stir, heat rapidly to boiling, and boil 1 minute after the foam disappears, or for any other fixed period up to 3 minutes. Cool rapidly to some fixed temperature below  $25^{\circ}C$ , the cooler the better, and titrate rapidly with sodium arsenite solution until the solution assumes a yellowish color or until 1 drop produces no further change in the color of the solution.

For special solutions required, see page 80.

### Application of the Method to Alloy Steels

As already indicated, the method is applicable without modification to all alloy steels except those containing more than 0.5 per cent tungsten or more than 1 per cent chromium. Preliminary treatment of the sample for each case is given separately as follows:

#### Treatment of Sample When a Preliminary Separation Is Not Required

Transfer the sample to a suitable flask or beaker (400 ml capacity) and dissolve with 25 ml to 30 ml of the nitric-sulphuric-phosphoric acid mixture, according to the weight of the sample used. If solution is slow, add 5 to 10 ml of water, or dissolve in 20 ml of dilute sulphuric acid (1:10) and add, following solution, 7 ml of nitric acid and 3 ml of orthophosphoric acid (85-per cent). Boil to expel oxides of

nitrogen, dilute to 100 ml with hot water, and complete the determination as described below under the heading *Oxidation and Titration of the Manganese*.

### **Rapid Method for High-Chromium, Stainless, and Heat-Resistant Steels**

The following method, submitted by Fred Wilson Smith,\* is extremely rapid, and has been proved accurate in the hands of different analysts in several laboratories. Although the separation of the chromium has been given under *Chemical Separations*, the complete procedure for manganese is given below since the method is new.

#### **Solution of the Sample and Elimination of Chromium**

To 1 g of the sample in a 500-ml Erlenmeyer flask, add 25 ml of a mixture composed of 1 part dilute HCl (1:4) and 4 parts  $\text{HClO}_4$  (72-per cent). Heat gently, preferably on a hot plate, and when solution is complete, increase the temperature and fume 5 to 10 minutes or until all the chromium is oxidized. To volatilize the chromium, add 1 to 4 g of NaCl in small portions, making the additions until the chromium content has been reduced to the point desired or until no noticeable fumes of  $\text{CrO}_2\text{Cl}_2$  are evolved. If it is desired to eliminate practically all the chromium, add the larger amount of NaCl.

#### **Oxidation of Manganese**

After the last addition of NaCl, boil the solution for 1 minute to free it of HCl. Add 30 ml of the nitric-sulphuric-phosphoric acid mixture (see page 81), 10 ml of a 1-per cent solution of  $\text{AgNO}_3$ , and 100 ml of hot water. Heat to boiling and add 10 ml of a 30-per cent solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Boil the solution for 30 seconds, cool rapidly, and titrate the permanganic acid formed with a standard solution of sodium arsenite.

#### **Treatment of Sample in the Presence of Much Chromium or Much Chromium and Tungsten**

Separate the greater portion of the chromium and tungsten, if the latter is present, by the bicarbonate, the zinc oxide, or the lead perchlorate methods as described in the preceding section on chemical separations. If the steel contains much carbon, as in the grades used for cutlery, tools, etc., test the residues and precipitates for manganese. To decompose residues completely, digest with  $\text{HNO}_3$  several times if necessary. To eliminate chlorides, if there has been a chance of their introduction, add 5 ml of  $\text{H}_2\text{SO}_4$ , evaporate to fumes, dilute slightly, add 4 ml of  $\text{H}_3\text{PO}_4$ , 8 ml of  $\text{HNO}_3$ , boil, cool, dilute to 125 ml, and treat as directed later for the oxidation of the manganese. If the

\* Unpublished report, February 12, 1937, South Works Laboratory, Carnegie-Illinois Steel Corporation, Chicago, Illinois.

solutions from the separations are neutral and free of nitrous fumes, organic matter, and chlorides, add 30 ml of the nitric-sulphuric-phosphoric acid mixture, dilute to 125 ml, and proceed with the oxidation of the manganese.

### **Treatment of Sample in the Presence of Tungsten With Chromium Absent or Under One Per Cent**

Dissolve 0.5 g of sample by either of the following methods:

1. If carbon is low (under 0.2 per cent), add 50 ml of dilute sulphuric acid (1:10) and 3 ml of orthophosphoric acid (85-per cent) and heat. When action has ceased, gradually add 5 ml of nitric acid to oxidize the carbides, dilute with 40 ml of water, and boil. Treat as directed below for the oxidation and titration of the manganese.

2. If carbon is high, add 10 ml of a mixture of equal parts of hydrochloric and nitric acids, and 4 or 5 drops of hydrofluoric acid. When action has ceased, add 5 ml of perchloric acid (60-per cent) and evaporate just to dryness. Cool, add 5 ml of sulphuric acid (sp. gr. 1.84), heat, and fume until *all chlorine compounds are expelled*. Cool, add 50 ml of water and 5 ml of orthophosphoric acid (sp. gr. 1.73), stir, dilute to about 100 ml, and heat until salts have dissolved, adding a few drops of freshly prepared  $\text{SO}_2$ -water if necessary to reduce and dissolve manganic compounds. Treat the solution for the oxidation and titration of the manganese as directed below.

3. A third method proposed involves solution of the steel in acid and separation of the manganese with ammonium persulphate in ammoniacal solution, but this method is not recommended for use in exacting work.

### **Oxidation and Titration of the Manganese**

Add to the chloride-free acid solution, as prepared by any of the methods described above, 5 ml of a 1-per cent solution of silver nitrate and 10 ml of a 30-per cent solution of ammonium persulphate or 30 ml of a saturated solution of potassium persulphate. Mix, heat rapidly to boiling, and boil briskly for 1 minute. Cool, preferably in running water, and titrate the permanganic acid with standard sodium arsenite solution until 1 drop dispels the red color, or until the addition of another drop produces no further change in the color.

If the end point should be overrun, reheat, add persulphate, and repeat the determination as before.

Multiply the ml of arsenite solution used by its manganese titer, times 100, and divide by the weight of sample used to find the per cent manganese.

### **Other Modifications of the Method**

Several modifications of this procedure have been proposed, but that above is the one now used generally. The reduction of the per-

manganic acid with sodium arsenite does not progress to the divalent stage, but can be made to go to this point by adding sodium nitrite to the arsenite solution in molecular proportions and by removing the silver ion with a slight excess of sodium chloride. This treatment makes it impossible to check over-titrations.

The titration may be made potentiometrically with the Larrabee or the Kelley apparatus. If the latter instrument is used, it is best to insert a salt bridge (a solution of  $\text{Na}_2\text{SO}_4$ ) between the calomel electrode and the titrating solution. The Larrabee apparatus is described as follows:

**The Larrabee Apparatus.**—The apparatus used consists essentially of a stirring apparatus, electrodes, and a potentiometric unit. The stirring apparatus is of the conventional type and requires no explanation. The electrodes consist of a pure gold and a pure platinum rod each with small vanes of the same metal at the bottom. The latest model of this patented apparatus is shown in Fig. 12, page 149. The two electrodes project into the solution, and are supported in correct position by the stirring apparatus. They are cleaned daily by immersing them in a hot saturated solution of potassium dichromate in concentrated sulphuric acid. The potentiometer consists of a dry battery with rheostat, galvanometer, and switches, all mounted in the case beside the burette support. With this apparatus the analysis is carried out as follows:

**Preparation of Sample for Titration.**—The sample is weighed, dissolved in the acid mixture, and treated for the oxidation of the manganese as described under *Procedure II—Visual Titration*, with the following exceptions: (1) When large percentages of manganese or chromium or both are present, the silver nitrate is increased to 10 ml and the persulphate to  $1\frac{1}{2}$  or 3 times as much. (2) If the proportion of manganese to be determined is extremely small, the amounts of persulphate and of silver nitrate are decreased to  $\frac{1}{2}$  or  $\frac{1}{3}$  as much. For example, for manganese under 0.02 per cent, 3 ml of persulphate and 2 ml of silver nitrate solution are sufficient; and these smaller additions avoid the blank, which is appreciable when the larger amounts of these reagents are used. (3) When these changes are made and the highest degree of accuracy is desired, the arsenite solution is standardized against a similar amount of manganese oxidized with the same amounts of silver nitrate and persulphate, and in the presence of relatively the same amount of iron. (4) The solution of the sample and subsequent oxidation of the manganese is conducted in a 600-ml beaker. (5) For highest accuracy, solutions are cooled to  $10^\circ\text{--}15^\circ\text{C}$  for titrating.

With the solution ready to titrate, the electrodes are connected externally with the insulated wires attached to the binding posts at the rear of the instrument panel. In making these connections no attention need be given to polarity. The beaker containing the solu-

tion to be titrated, cooled to between 15° C and 20° C, is placed on the support and its position is adjusted so that the electrodes and stirring propeller are immersed in the solution to almost full depth. The stirring motor is started, and its rheostat is adjusted so that its speed is as great as possible without danger of spattering the solution. The standard sodium arsenite solution is added from the burette as rapidly as possible until the purple color begins to fade. At this point the handle of the switch at the right of the galvanometer scale is pushed toward the back of the instrument. An attempt is made to balance the galvanometer by turning the knob on the front of the panel. If the galvanometer needle persists in pointing to one side of the center of the scale, the handle of the switch is pulled toward the front of the case, and the knob is turned until the needle remains over the center of the scale. The standard sodium arsenite solution is now added slowly and in smaller and smaller portions, a few seconds time being given after each addition for the galvanometer needle to return to the center of the scale. When the addition of 1 drop of the sodium arsenite solution produces a permanent deflection of the galvanometer needle, the stirring motor is stopped and the burette reading is recorded.

It should be noted that the word "permanent" above is used in a relative sense, as the needle will always return to zero if given sufficient time, due to the fact that the manganese is slowly reoxidized even in the cold.

From the number of ml of sodium arsenite used, the per cent manganese is computed by multiplying this number by 100 times the manganese value of the arsenite solution, and dividing by the weight of sample used.

### Solutions and Special Reagents Required

**Silver Nitrate Solution (1-per cent).**—Dissolve 10 g  $\text{AgNO}_3$  in 1000 ml  $\text{H}_2\text{O}$ .

**Ammonium Persulphate Solution (30-per cent).**—Dissolve 30 g of ammonium persulphate assaying 95 per cent  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in 100 ml of water, and use while fresh.

**Standard Sodium Arsenite Solution.**—Prepare a stock solution by dissolving 22 g in 1000 ml of water, allow to age 3 weeks, and dilute 100 ml to 1000 ml for use as needed. This procedure gives a stable solution. With a few trials the stock solution can be used to make up solutions of the exact concentration required to give a solution 1 ml of which is equivalent to 0.1 per cent on a 0.5-g sample. For this purpose the stock solution is best measured with a weight burette.

The sodium arsenite is generally standardized against standard steels, similar in composition to the steels to be analyzed. The standard is run through all steps of a regular determination, and the

arsenite solution is adjusted so that 1 ml = 0.1 per cent of manganese on a sample of 0.5 g.

**Nitric-Sulphuric-Phosphoric Acid Mixture.**—Add 185 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) to 440 ml  $\text{H}_2\text{O}$ , then add 125 ml of  $\text{H}_3\text{PO}_4$  (85-per cent) and 250 ml  $\text{HNO}_3$  (sp. gr. 1.42).

### SODIUM BISMUTHATE METHOD

#### Application of the Method

While the sodium bismuthate method is generally accepted as a reference method for manganese, it requires great care to obtain accurate results. Compounds that interfere are oxides of nitrogen, hydrochloric acid, chlorides, hydrofluoric acid, large proportions of phosphoric acid, and practically all organic compounds. Elements that interfere are cerium, cobalt, chromium, vanadium, and very high percentages of nickel, the last only if the manganese is titrated visually. When either of the first two are present, they must be separated previous to applying the method, as they are oxidized by the bismuthate and are subsequently reduced with the permanganic acid, except as noted below. By the usual method of titrating the permanganic acid with ferrous sulphate and permanganate, following oxidation with bismuthate, small proportions of chromium (up to 0.5 per cent) and vanadium (up to 0.25 per cent) do not affect results seriously if the delayed end point caused by the latter is recognized, but larger proportions should be separated by one of the methods given in the section on *Separations*, preferably the bicarbonate, zinc oxide, or lead perchlorate method. If the chromium is volatilized,  $\text{HCl}$  instead of  $\text{NaCl}$  should be used and care taken to fume off all of the former. By titrating the permanganic acid with sodium arsenite solution, interference by cerium is overcome and chromium up to 3 per cent is permissible. Large percentages of nickel (over 30 per cent) offer some color interference at the visual end point, which can be partly overcome by adding pure cobalt nitrate.

#### Weight and Treatment of Sample

**Blank.**—One gram of sample may be used for all steels, except the high-manganese steels, for which 0.5 g or less must be used. The initial treatments for other alloy steels are briefly outlined below.

In all analyses a blank should be carried through all steps, using all reagents and omitting only the sample.

**Treatment of Sample in the Presence of Cobalt.**—Use 1 g of sample and separate the manganese, preferably by the improved chlorate (Ford) method, as directed in the section on separations. As an alternate separation, use the perchloric acid-ammonia-ammonium persulphate method.



Make sure that all traces of chlorine compounds are expelled before proceeding with the oxidation treatment with bismuthate.

**Treatment of Sample in the Presence of Tungsten.**—In the absence of cobalt, use 2 g of sample and make a zinc oxide separation as described under *Chemical Separations*. After filtering and aliquoting, heat the solution to boiling, add 5 ml of the acid (preferably  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ), and boil down to about 75 ml. Treat this solution as described below for the oxidation of the manganese with bismuthate.

In the presence of both cobalt and tungsten, a second separation is necessary, either of the cobalt by treatment with sulphide, or of the manganese by acidifying, adding ammonia, and precipitating with ammonium persulphate or applying the chlorate method. Neither separation is as accurate as desired, and the persulphate arsenite method is not entirely satisfactory for use when much cobalt is present.

**Treatment of Sample in the Absence of Cobalt and Presence of Much Chromium, Phosphorus, or Nickel.**—For chromium under 3 per cent, use 1 g of sample, treat as directed below, and titrate the permanganic acid with standard sodium arsenite solution.

If the chromium is over 3 per cent and phosphorus and nickel are normal, use 2 g and apply the zinc oxide separation, or use 1 g and separate the chromium with sodium bicarbonate or lead perchlorate.

In the presence of large proportions of phosphorus or nickel, or both, use 1 g and separate manganese in oxidized solution with sodium bicarbonate or by the improved chlorate method.

**Treatment of Sample When a Preliminary Separation is Not Required.**—Dissolve 1 g of the sample in 50 ml of dilute nitric acid (sp. gr. 1.135), and boil to the expulsion of oxides of nitrogen. Cool somewhat and add sodium bismuthate (0.5 g at first) until a pink color develops or the oxide of manganese precipitates. Boil 2 minutes and add a freshly prepared solution of  $\text{SO}_2$  until the solution is clear. Boil until oxides of nitrogen and sulphur are expelled, and treat as described below for determination of the manganese.

### Oxidation of the Manganese with Bismuthate

If the sample is in nitric acid solution, oxidize it as described above. If the sample is in sulphuric acid solution, heat to boiling, add ammonium persulphate first, and finally, a very small quantity of sodium bismuthate. Then, reduce with  $\text{H}_2\text{SO}_3$  and boil as directed above. If the sample is in perchloric acid solution following the lead perchlorate separation, add nitric acid to 15 per cent, and omit the preliminary oxidation with bismuthate or, preferably, preoxidize and reduce as directed in the preceding paragraph.

With the solution thus thoroughly oxidized and the acidity properly adjusted (15 to 20 ml of  $\text{HNO}_3$  or 5 to 10 ml of  $\text{H}_2\text{SO}_4$  per 100 ml), cool to below  $20^\circ \text{C}$  (better  $15^\circ \text{C}$ , or to  $10^\circ \text{C}$  if Cr is present), and

add an excess of sodium bismuthate, at least 25 times as much as the weight of the manganese present. Stir vigorously, and if all or nearly all the bismuthate added should dissolve, add more immediately. Let the solution stand 1 minute and add 50 ml of a 3-per cent nitric acid solution (free of nitrous acid) and filter preferably through a purified asbestos pad, or a glass frit or alundum crucible, sufficiently tight to prevent passage of bismuthate particles. With glass frit or alundum, care is required to guard against clogging or passing of bismuth through the filter. Wash the filter 3 or 4 times with the nitrous-free 3-per cent  $\text{HNO}_3$  solution, and titrate the solution by one of the following methods, as required by circumstance or the composition of the sample.

**A. Ferrous Sulphate-Permanganate Titration.**—If the sample is in sulphuric or nitric acid solution, add 2 ml of orthophosphoric acid to the filtrate, and stir. In perchloric acid solution omit the phosphoric acid. Add from a burette standard ferrous sulphate solution until the pink color is discharged, and 1 to 2 ml excess. Back-titrate this excess with standard potassium permanganate solution until one drop gives a distinguishable pink end point. If vanadium is present, the end point will be a fading one, and to avoid error, add the permanganate until the end point persists for at least 1 minute.

To ascertain the blank due to color interference, if the solution is colored, boil the solution 10 minutes. Cool to the same temperature as before, and titrate again to the same end point. If this titration requires more of the permanganate than is required to give an end point in a colorless solution, subtract the difference from the ml of permanganate used in the titration.

Titrate the blank to the same end point with the permanganate solution as a check on reagents used. Then, add the same volume of the ferrous sulphate solution as was used in the determination, and titrate with the permanganate, noting the ml of the latter added in both titrations..

The difference in the volumes of the  $\text{KMnO}_4$  solution used in the two titrations represents the manganese in the sample. From the normality, calculate the per cent manganese.

**B. Titration with Standard Sodium Arsenite Solution.**—Titrate the solution to a clear greenish yellow color which does not change on adding another drop of the arsenite. From the manganese titer of the solution, calculate the per cent manganese.

### Solutions and Special Reagents Required

**Apparatus.**—200- and 400-ml beakers, 2 accurately calibrated 50-ml burettes, heaters, and suction filtering equipment.

**Dilute Nitric Acid (sp. gr. 1.135).**—Dilute 255 ml of  $\text{HNO}_3$  (sp. gr. 1.42) with 770 ml water.

**Dilute Nitric Acid (3-per cent).**—Must be free of nitrous fumes. Boil 40 ml of the concentrated acid; cool, and bubble clean pure air through it for 5 minutes; dilute to 1000 ml, add 1 g sodium bismuthate, and allow to settle. Keep in a cool dark place.

**Asbestos Filter.**—Shred asbestos; ignite gently; digest with HCl; wash with  $H_2O$  in a ribbed funnel with platinum cone; digest 5 hours with  $HNO_3$  (1:3); wash thoroughly with hot  $H_2O$ , and mix with water. To make filter, use a carbon filter tube. Add enough asbestos suspension to make a thin tight filter, apply suction gently, and wash thoroughly with hot water, and the 3-per cent nitric acid above. Then wash with  $KMnO_4$  solution and with the dilute  $HNO_3$  till the washings are colorless. Note that the same pad cannot be used for more than 3 to 5 filtrations, as the bismuthate gradually penetrates even the best-made pads.

**Bismuthate.**—Must contain active  $O_2$  equivalent to 75 per cent  $NaBiO_3$ , and be free of Mn and Cl. The salt is tested for Cl ion by dissolving in dilute  $HNO_3$  with the aid of  $SO_2$  and adding a solution of  $AgNO_3$ ; for manganese, a blank analysis is made on a weighed portion of the salt. To assay, dissolve 0.7 g in 20 ml of water containing 1.75 g of  $FeSO_4 \cdot 7H_2O$  and 5 ml dilute  $H_2SO_4$  (1:1). Shake at intervals for 30 minutes, and titrate the excess ferrous sulphate with 0.1  $N$   $KMnO_4$ . Find the  $KMnO_4$  equivalent to the  $NaBiO_3$  used. 1 ml of 0.1  $N$   $KMnO_4$  = 0.014 g  $NaBiO_3$ .

**Ferrous Ammonium Sulphate.**—Dissolve 12 g  $Fe(NH_4)_2(SO_4)_2$  in a cold solution of 50 ml  $H_2SO_4$  (sp. gr. 1.84) in 950 ml  $H_2O$ .

**Standard Potassium Permanganate Solution (0.03 N).**—Dissolve 1 g KOH in 1000 ml of water and add 1 g  $KMnO_4$ . Age 1 week and filter through purified asbestos pad. Dissolve 0.1 g of Bureau of Standards sodium oxalate in 100 ml of boiled and cooled 5 per cent  $H_2SO_4$  solution. Add  $KMnO_4$  solution with constant stirring to a faint pink color. Heat to  $70^\circ C$  and titrate with  $KMnO_4$  solution, stirring constantly and adding the solution, dropwise, to a lasting pink end point. Titrate a blank  $H_2SO_4$  solution in the same way, and subtract this blank from the ml  $KMnO_4$  solution used to titrate the oxalate. Calculate the manganese value of 1 ml of the  $KMnO_4$  solution. A normal solution of sodium oxalate equals 67 g per liter and 1 ml of  $N$   $KMnO_4$  equals 0.01099 g Mn, or 1 ml of 0.03  $N$  equals 0.0003296 g Mn.

**Standard Sodium Arsenite Solution.**—Dissolve two grams of pure sodium arsenite in water, filter if necessary, and dilute to 1 liter, or use stock solution as given under persulphate method. Standardize against 20 ml portions of the standard  $KMnO_4$  solution in 100 ml of the filtered 3-per cent  $HNO_3$  solution, to a clear greenish yellow end point, or against standard steels, one containing no chromium and the others about the same as the steels to be analyzed.

### **Oxidation of the Manganese in Sulphuric Acid Solution Followed by Potentiometric Titration**

Since the end point is obtained electrometrically, the following method is applicable to irons containing large percentages of chromium and requires no separation of this element. The procedure is as follows:

Transfer 1 g of sample to a 200-ml Erlenmeyer flask and dissolve it with 60 ml of dilute sulphuric acid (1:9), the action of the acid being hastened by the application of gentle heat. Separate any insoluble matter by filtration and wash it with hot water until it is free of acid. Ignite the filter and residue in a platinum crucible, and volatilize the silica present by adding 1 or 2 drops of dilute sulphuric acid (1:1) and 3 to 4 ml of hydrofluoric acid to it, and evaporate to dryness. Ignite the residue gently and fuse with a little potassium pyrosulphate. Dissolve the fusion in water and add to the filtrate, which is treated with 5 g of ammonium persulphate, and boiled for 10 to 12 minutes to oxidize iron and other elements and destroy combined carbon. To reduce any oxidized chromium, permanganic acid, or manganese dioxide that may have been formed, add sulphurous acid dropwise until the solution shows no further change in color; and expel the excess sulphite by continuing the boiling for 5 minutes. Cool the solution to 15° C or below and treat with an excess of sodium bismuthate (0.5 to 1 g according to the manganese present). Agitate the mixture thoroughly for 1 to 2 minutes, employing a longer time if the temperature is below 10° C. Filter the solution through an asbestos mat prepared as described below, and wash the filter with ice-cold 3-per cent sulphuric acid until the washings are colorless. To avoid any chance of permanganate oxidizing a little chromium, the solution must be kept cold and the manganese titrated without delay. Therefore, dilute the acid solution immediately with water at the same temperature to a volume between 250 and 300 ml, and titrate the manganese with sodium arsenite solution using the Larrabee potentiometric titration apparatus.

The sodium arsenite is standardized against potassium permanganate which is added to the same volume of water containing the same proportion of acid as is used in the determination.

### **THE GRAVIMETRIC PHOSPHATE METHOD**

This method, seldom used except as a check under unusual conditions, is adaptable to large or small proportions of manganese but requires a preliminary separation of the manganese from all other elements precipitated as phosphates in alkaline solution. For this purpose, the chlorate method given in the section on separations is generally used. By this combination, the procedure following the separation, subsequent to the removal of tungsten, if present, is as follows:

### Procedure

Dissolve the  $\text{MnO}_2$  on the filter pad before it is washed with water, and as directed in the separation, or with ammonium bisulphite solution and boil free of  $\text{SO}_2$ . Cool the clear solution and add ammonia until a slight permanent precipitate forms. Add 15 ml of a 20-per cent solution of ammonium acetate, and boil 2 minutes. Filter the solution into an 800-ml beaker, and wash the filter twice with hot water. Dissolve the precipitate with hot dilute hydrochloric acid (1:1) into the beaker in which the precipitation was effected, repeat the precipitation, and filter into the 800-ml beaker containing the first filtrate.

To the combined filtrates, add 5 ml of acetic acid and 10 ml of a 10-per cent solution of ammonium phosphate. Heat the solution to the boiling point and add ammonia slowly with constant stirring until a permanent opalescence appears. Continue the stirring vigorously until the characteristic salmon-colored crystalline precipitate of ammonium manganese phosphate is well defined. Then, continue the addition of ammonia dropwise until a total of 25 ml has been added. Remove the beaker from the heat, cover it, and let it stand until the precipitate has settled. Collect the precipitate upon an 11-cm filter paper and wash 3 or 4 times with a solution of ammonia and ammonium nitrate (water 760 ml, ammonia 200 ml, and nitric acid 40 ml). Ignite the paper and precipitate in a weighed porcelain crucible at a low temperature until the paper is burned, then at  $900^\circ$  to  $1000^\circ\text{C}$  for 15 minutes. Cool in a desiccator and weigh. Dissolve the precipitate in the crucible with hot dilute  $\text{HCl}$  (1:2), filter, wash thoroughly with dilute  $\text{HCl}$  (2-per cent) and water, reignite the filter in the same crucible, and weigh as  $\text{SiO}_2$  and other acid-insoluble impurities. Subtract this weight from the previous weight to find the weight of pure manganese pyrophosphate, then multiply by 38.69, and divide by the weight of sample used to find the per cent Mn present.

# Determination of Phosphorus

## Methods Available

Among the first methods for phosphorus in steel is that described by Fresenius and later designated as the acetate method. The only other practicable method known for separating phosphorus in the analysis of steel is that in which it is precipitated as ammonium phosphomolybdate, a yellow compound of variable composition. The former can still be used to advantage occasionally, but the latter is used almost universally. In reality, the molybdate method constitutes a selective separation of the phosphorus provided certain conditions are maintained and interfering elements are absent. After the phosphorus has been all gathered in the yellow precipitate, its determination may be made in several different ways. Thus, if the yellow precipitate is obtained pure, it may be dried and weighed direct, or the phosphorus may be found by methods based on its reaction with an alkali, on the reduction of the phosphomolybdate and titration of the molybdenum, or on the solution of the yellow precipitate followed by reprecipitation of the molybdenum as lead molybdate or of the phosphorus as magnesium phosphate. The alkali and the magnesium ammonium phosphate methods are the ones generally used. Also, with practice, the phosphorus, if present in small proportions, can be estimated visually from the turbidity caused by the precipitate. It is, therefore, important to study the conditions of this precipitation with care.

## THE MOLYBDATE METHOD

### General Precautions

Conditions most favorable to the separation with molybdate are:

1. The phosphorus must be completely oxidized to orthophosphoric acid. This oxidation must be effected, at least in part, during solution of the sample. Hence, speaking of metallic alloys in general, the sample must be dissolved in an oxidizing acid or under oxidizing conditions to avoid the chance loss of the element as phosphine.
2. The precipitation is generally effected in a nitric acid solution of the steel, free of organic matter and other interfering substances, containing 5 to 8 per cent free nitric acid and more than 5 per cent ammonium nitrate. Perchloric acid and ammonium perchlorate do not interfere and may be substituted for a part or all of the nitric acid.
3. The ammonium phosphomolybdate precipitating reagent should be added in such quantity as to give an excess of 1.5 g of  $\text{MoO}_4$  ion per 100 ml over that required to precipitate the phosphorus present.

4. The temperature of the solution after the addition of the ammonium phosphomolybdate solution should be between 40° C and 50° C.

5. The solution should be shaken vigorously after the addition of the phosphomolybdate for 5 to 10 minutes and cooled before filtering; C. E. Nesbitt has shown that long standing after precipitation is not necessary, if the solution is shaken as stated and cooled to below 20° C.

6. The precipitate should be washed sparingly with a 1-per cent solution of nitric acid, and then with a 5-per cent solution of ammonium nitrate. Its solubility in order is: alkaline solutions (completely or very soluble), concentrated nitric acid, water, 1-per cent nitric acid, 1-per cent potassium nitrate, 1-per cent acid potassium sulphate, 5-per cent neutral ammonium nitrate—insoluble. From this list, a wash solution suitable to the subsequent treatment is selected.

Interfering substances are listed as follows:

1. Precipitation of the phosphorus is retarded by vanadium, tungsten, titanium, zirconium, silica, and arsenic and by sulphuric acid, hydrofluoric acid, hydrochloric acid, the ammonium salts of these acids, and some organic compounds; also, by precipitating in the cold and failure to shake after adding the ammonium molybdate solution.

2. If arsenic, vanadium, tungsten, or silicon are present, they are partly precipitated or otherwise carried down with the precipitate. Vanadium in the quadrivalent state is not precipitated, but retards the precipitation somewhat.

3. Titanium and zirconium retard precipitation and cause low results by forming insoluble titanium and zirconium phosphates, which may remain with the  $\text{SiO}_2$  or  $\text{SiO}_2$  and  $\text{WO}_3$ , or fail to be dissolved with the ammonium phosphomolybdate.

With these facts in mind, reasons for the various steps and precautions in the following procedures will be apparent from the composition of the steels to be dealt with. Since analyses must frequently be started without knowledge of the composition of the steel, the following methods are classed according to the solubility of the steels. However, as a means of defining the proper conditions for the precipitation of the phosphorus, the procedure applicable to steels practically free of interfering elements is given first.

### Solution of the Sample and Precipitation of Phosphorus

**Weight of Sample.**—In general, phosphorus in steel may vary from 0.003 per cent to 0.175 per cent, depending upon the process of manufacture, the kind and type of steel, and the purpose for which it is intended. In an analysis, small proportions, as a rule, cannot be as accurately estimated as larger proportions, particularly by gravimetric methods. Therefore, the weight of sample is varied as follows:

When the phosphorus is to be determined by volumetric methods, use 1 g for phosphorus over 0.100 per cent, 2 g for 0.010 to 0.125 per cent, and 3 g when the phosphorus is under 0.010 per cent.

For the gravimetric methods, larger samples should be used—6 to 10 g, when the phosphorus is under 0.010 per cent, and 3 to 6 g for all other steels.

With such large samples, the separation of the phosphorus sometimes becomes very troublesome, but this objection is overcome by using two approximately equal portions, and either collecting the yellow precipitates on the same filter or combining the solutions after the precipitates have been collected, washed, and redissolved.

**Procedure for Dissolving Steels Containing Little or No Silicon,  
Titanium, Tungsten, Uranium, Vanadium, Zirconium,  
Columbium, or Tantalum**

**Carbon- and Low-Alloy Steels Soluble in Nitric Acid**

Transfer 2 g (3 g or 4 g if P is under 0.010 per cent) to a 300-ml Erlenmeyer flask, add 50 ml of dilute  $\text{HNO}_3$  (sp. gr. 1.20), and heat gently. When the sample has dissolved, add a 2.5-per cent solution of potassium permanganate until there is a slight excess (3 to 10 ml) and boil for 2 or 3 minutes to complete the oxidation of the solution. Add a solution of sodium sulphite or nitrite, a solution of phosphorus-free sugar (cane sugar), or a freshly prepared solution of sulphur dioxide drop by drop until the precipitate just dissolves, and continue the boiling for 1 or 2 minutes to expel all oxides of nitrogen and sulphur. Cool to about 70° C (some prefer to cool only to 90° to 95° C) and add 50 ml of the ammonium molybdate solution. Stopper the flask, shake vigorously for 5 to 10 minutes, preferably mechanically, cool to 20° C or below, and filter through a close paper. Rinse the flask and wash the paper and precipitate twice with about 5-ml portions of a 10-per cent (2-per cent can be used) solution of nitric acid. If phosphorus is to be determined volumetrically, rinse and wash as before 2 or 3 times with a 1-per cent solution of potassium or sodium nitrate; and finally wash the paper and precipitate 9 or 10 times to remove excess acid, exercising due care to prevent the precipitate from creeping over the edge of the paper.

If phosphorus is to be determined gravimetrically by the more accurate phosphate method, wash the precipitate 5 times only with a 2- to 5-per cent solution of ammonium nitrate. If the yellow precipitate is to be dried and weighed, as when extreme accuracy is not required, wash it 6 to 8 times with 2-per cent nitric acid only, dry at 120° C, and weigh it rapidly, because the salt is hygroscopic. The dried precipitate contains 1.65 per cent phosphorus.

**High-Manganese Steels**

Dissolve 4 g of the sample in 70 ml of dilute nitric acid (sp. gr. 1.135), then add 35 ml of perchloric acid (60-per cent), and evaporate to fumes. To remove silica, add hydrofluoric acid dropwise until 3 to



5 drops excess has been added. Heat till the perchloric acid is refluxing on the sides of the container, and maintain this temperature for 25 to 30 minutes. Cool, add 50 ml of water, 10 ml of nitric acid, and 2 or 3 drops of a 2-per cent solution of potassium permanganate. Boil till all the permanganic acid is converted to oxide and dissolve by adding a solution of  $\text{SO}_2$  until the solution is clear. Boil to expel all fumes of oxides of nitrogen or sulphur. Cool to  $70^\circ \text{C}$  and complete the separation as directed above.

### Solution of Steels Insoluble in Nitric Acid

**High-Chromium Stainless and Heat-Resistant Steels.**—*Weight of Sample.* If the phosphorus is to be determined volumetrically, 2 g of sample are generally used. When the phosphorus is to be weighed as magnesium pyrophosphate, a sample of 4 g or more should be used, and the amount of perchloric acid increased accordingly to give the same acidity after solution, or two or more portions may be run through as directed and the precipitates combined.

*Procedure A.*—For dissolving steels included under this heading, mixtures of  $\text{HCl}$  and  $\text{HNO}_3$  and of  $\text{HCl}$  and  $\text{HClO}_4$ , also  $\text{HClO}_4$  alone, have been used. In using these mixtures, we have frequently had low results, due apparently to loss of phosphorus from the manner in which the  $\text{HCl}$  is added. With the  $\text{HCl}$ - $\text{HNO}_3$  mixture, it is necessary to mix the acids in the proportion of 1  $\text{HCl}$  to 2  $\text{HNO}_3$  several hours before using. With the  $\text{HCl}$ - $\text{HClO}_4$  mixtures, low results are frequently obtained, so that it is safest to dissolve the sample in the  $\text{HCl}$ - $\text{HNO}_3$  mixture (30 ml for a 2-g sample) and then add the  $\text{HClO}_4$  (30 to 40 ml of 55-per cent  $\text{HClO}_4$  for a 2-g sample). If much vanadium is present, low results may be expected; if vanadium is absent or present in small percentages, the following procedure gives results satisfactory for routine work.

Transfer the sample to a covered 400-ml beaker and dissolve it in the  $\text{HCl}$ - $\text{HNO}_3$  and add  $\text{HClO}_4$  as explained above, using more of the latter if chromium is high. Evaporate to fumes and continue the heating until all the chromium is oxidized or for 5 minutes after  $\text{HClO}_4$  has begun to condense on the wall. Cool, add 50 ml of water, and filter to eliminate silicon and columbium, if present in troublesome amounts. Add a saturated solution of  $\text{SO}_2$  till all the chromium and vanadium are reduced, and boil until all the  $\text{SO}_2$  has been expelled. Cool the solution to  $90^\circ \text{C}$  to  $95^\circ \text{C}$ , add 40 ml of ammonium molybdate solution, and shake for 5 minutes. Filter the solution, wash the filter and yellow precipitate in the usual manner, and determine the phosphorus by titration with  $\text{NaOH}$  as described later or gravimetrically by the magnesia method. If vanadium is present, let the solution stand several hours after precipitating the phosphorus, and if a large residue is filtered off after solution in the acids, fuse it as directed below.

Ignite the residue gently in a weighed platinum crucible, and if it weighs more than 1 mg, moisten with hydrochloric acid; add hydrofluoric acid, evaporate to dryness, and fuse with a little sodium carbonate, if the weight still exceeds 1 mg. Leach with about 10 ml of water and filter through a close filter, adding filtrate and washings to the original filtrate. As an alternate procedure, add 10-per cent solution of NaOH, boil 10 minutes, dilute, and filter.

*Procedure B.*—The following procedure, using  $\text{HClO}_4$  alone, has been carefully investigated by us and others<sup>1</sup> and found to give satisfactory results on all types of stainless steels including those containing selenium, titanium, silicon, zirconium, and vanadium, the phosphorus being determined either by titrating with sodium hydroxide or by weighing as the pyrophosphate. The method is not applicable to certain other types of steel, and its use is best restricted to the stainless steels. The procedure recommended is as follows:

Transfer the sample (2 g or more if the phosphorus is to be weighed as magnesium pyrophosphate) to a 500-ml Erlenmeyer flask, and dissolve by adding 20 ml (for 2 g) of 60-per cent perchloric acid and warming gently. Cover the mouth of the flask with a small short-stem funnel and boil till the chromium is all oxidized (20 to 30 minutes) when the solution will assume a deep red to brown color. If much residue remains, dilute, filter, wash, and fuse it as directed above. If the acid-insoluble matter is small in amount, cool, dilute to 100 ml, and add ammonia (10 ml or more) until a slight precipitate forms, and dissolve with 20 to 25 ml of nitric acid (sp. gr. 1.20). Add a solution of ammonium bisulphite (1:10) or of ferrous ammonium sulphate, mixing thoroughly after each addition, until the chromium and vanadium compounds are reduced. Boil free of nitrous oxide and chlorine. Cool to between 60° C and 70° C, or lower if vanadium is present, mix in 50 ml to 60 ml of ammonium molybdate solution, cool rapidly to 20° C or below, and agitate, preferably mechanically, for 5 to 10 minutes.

Allow the precipitate to settle, at least for 30 minutes to one hour, or longer, if vanadium is present. Filter the solution and wash the precipitate 5 to 10 times with 2-per cent nitric acid. If the phosphorus is to be determined by titration with an alkali, continue the washing with a 2-per cent solution of sodium or potassium nitrate till it is free of acid. Complete the determination by one of the methods described later.

#### Steels Containing Much Silicon, Titanium, Tungsten, Uranium, Vanadium, Zirconium, Columbium and Tantalum

#### Weight and Solution of Sample

Use 2 g of sample (4 g if P is known to be under 0.010 per cent) and dissolve with a mixture of hydrochloric and nitric acids, as directed

for steels insoluble in nitric acid. As an alternate procedure, add the nitric acid first and the hydrochloric acid gradually until solution is effected, not forgetting that phosphorus may be lost if this order is reversed. After all the steel has dissolved, continue the boiling and observe the residue, if any, closely.

Any insoluble residue may consist of silica, tungstic acid, tungsten, chromium, columbium, or tantalum carbides, titanium and zirconium phosphates, and phosphotungstic acid. Tungsten, if present in appreciable amounts, will be obtained as a yellow residue and can be easily recognized.

In the apparent absence of tungsten, add 25 ml of perchloric acid, fume, dilute, filter, and treat the residue as directed in the preceding section, finally precipitating the phosphorus as directed below.

In the presence of tungsten, continue the evaporation to dryness. Add 20 ml of dilute hydrochloric acid (1:1), dilute to 100 ml with hot water, filter the solution, and wash the residue with water. Reserve the residue to test for phosphorus, as described later.

Add 30 ml of nitric acid to the filtrate and washings and evaporate to a syrup. Repeat this evaporation with nitric acid, if it is thought advisable in order to dispel all the hydrochloric acid, and take up with 50 ml of dilute nitric acid (sp. gr. 1.20). Filter off any insoluble residue, wash with water, and add it to the first residue.

### Precipitation of Phosphorus

In the presence of vanadium, cool the solution to between 10° C and 15° C and add 5 ml of a 40-per cent solution of ferrous sulphate to reduce vanadium to the quadrivalent stage. Stir, add a few drops of a fresh solution of SO<sub>2</sub>, stir, add 75 ml of the molybdate solution, shake vigorously for 10 minutes, and let stand for 4 hours or longer. Filter and wash the precipitate as directed for steels soluble in nitric acid. In the absence of vanadium, the precipitation and separation of the phosphorus may be carried out as directed in the preceding section for carbon steels and stainless steels.

### Treatment of Residues

The residues may contain a small part of the phosphorus. If the residue appears to be composed mainly of tungstic acid, it may be treated as follows: With a fine jet of water, wash most of the precipitate into a 100-ml Erlenmeyer flask, and treat the paper with 25 ml of hot dilute ammonia (1:4) to which 0.5 g citric acid has been added, collecting the latter in the Erlenmeyer flask to dissolve the main portion of the precipitate. Wash the paper twice with hot water, and 3 or 4 times with hot dilute hydrochloric acid (1:20), and acidify the solution with hydrochloric acid, keeping the volume under 75 ml. Ignite the papers, and if the residue is appreciable, treat it as described below.

If the residue contains much silica, ignite the papers gently to burn the carbon. Moisten the ignited residue with dilute hydrochloric acid (1:1), add hydrofluoric acid, and evaporate to dryness. Fuse with a little sodium carbonate, leach with water, and filter or digest with 10 ml of a 10-per cent sodium hydroxide solution, dilute, and filter. Acidify the solution with hydrochloric acid, add 2 or 3 ml of ammonia, 0.5 g of citric acid, and make slightly acid again, holding the volume under 75 ml.

To the slightly acid solution add 25 ml of acid magnesia mixture, cool in ice water, and drop in a few glass beads. Now, add ammonia till neutral and about 10 ml excess. Shake mechanically for 1 hour and let stand for 12 hours at a temperature under 5° C. Filter, wash 3 or 4 times with dilute ammonia, and complete the recovery by any one of the following optional procedures:

(a) Dissolve the precipitate with a little hot dilute nitric acid, and add it to the main solution of the sample before adding ammonium molybdate.

(b) Dissolve as in (a), add ammonium molybdate solution, shake, and determine phosphorus as usual.

(c) Dissolve the precipitate with a minimum quantity of hot dilute hydrochloric acid (1:4), reprecipitate with magnesia mixture, and weigh separately.

#### Treatment of the Yellow Precipitate for Estimation of Phosphorus

Complete the determination of the phosphorus by one of the following methods, using the gravimetric method only for referee work and in the analysis of standards.

**Alkalimetric Method.**—Transfer the properly washed paper and yellow precipitate to a titrating tumbler or return it to the flask in which the precipitation was made, first making sure that the titrating vessel is absolutely free of either acid or alkaline substances. Add 25 ml of CO<sub>2</sub>-free water and 5 ml of the standard sodium hydroxide solution.

Macerate the paper thoroughly with a glass rod or by shaking the flask. If the precipitate does not all dissolve, add 3 to 5 ml more of the sodium hydroxide solution, and so continue until an excess of 2 to 5 ml has been added. Add 100 ml of CO<sub>2</sub>-free water, 3 or 4 drops of phenolphthalein indicator, and standard nitric acid solution from a burette until the pink color is just discharged; this point is ascertained by adding 1 drop of the standard sodium hydroxide solution, which should restore the pink color. As a substitute for phenolphthalein, use a mixture composed of equal parts of neutral bromthymol blue and phenol red. For high phosphorus, use this mixture always, because these indicators have the advantage that they are more sensitive in the presence of much ammonia formed by a large amount of yellow precipitate.

Subtract the ml of acid used from the ml of the standard sodium hydroxide solution. Multiply the difference by the phosphorus titer of 1 ml of the sodium hydroxide solution, times 100, and divide by the weight of sample used to find the per cent phosphorus.

The calculations are simplified by standardizing the sodium hydroxide solution so that 1 ml equals 0.01 per cent phosphorus, and the concentration of the acid is adjusted so that 1 ml equals 1 ml of the alkali solution. Some chemists prefer to have 1 ml of the acid equal 0.01 per cent phosphorus, and the caustic soda solution somewhat more concentrated. Also, a few prefer to titrate to a colorless end point instead of a pink end point. These are optional details of procedure satisfactory for routine work, provided the same procedure is followed exactly not only in each determination, but also in standardizing the solutions.

**Gravimetric Magnesia Method.**—Mix and reserve the filtrate and washings from the yellow precipitate, set aside for 4 or 5 hours, and observe for any further precipitation of phosphorus.

Dissolve the yellow precipitate on the paper, as well as any remaining in the flask in which the phosphorus was precipitated, with 20 ml of dilute ammonia (1:1) to which has been added 2 g of citric acid, collecting the solution in a 250-ml beaker. Wash the paper several times with dilute ammonia (1:20), hot water, and dilute hydrochloric acid (1:20).

If the solution is not clear, indicating titanium or other interfering agents, heat it to boiling, filter through the same paper, wash the latter with hot water and burn off the carbon in a small crucible. Then, fuse this residue with not more than 0.5 g of sodium carbonate, leach with hot water, and filter into the main solution.

Add hydrochloric acid to the ammoniacal solution until it is slightly acid and evaporate, if necessary, to a volume of not more than 60 ml. Add 20 ml of magnesia mixture, stir, cool, preferably in ice water, and stir in ammonia until the solution is strongly ammoniacal. Stir the solution vigorously for at least 5 minutes, add 10 ml of ammonia, and let the solution stand in a cool place for at least 4 hours, and preferably 8 or 10. Filter on a close paper and wash the beaker and the filter 2 or 3 times with dilute ammonia (1:20). Discard the filtrate and place the beaker in which the precipitation was made under the funnel. Dissolve the precipitate on the filter with not more than 20 ml of hot dilute hydrochloric acid (1:1), and wash the filter once or twice with water.

If a yellow precipitate has appeared in the filtrate and washings from the first yellow precipitate, filter it off, wash thoroughly with 5-per cent ammonium nitrate solution, dissolve with dilute ammonia, and add it to the hydrochloric acid solution at this point.

If the presence of arsenic is suspected, it is eliminated through volatilization by treating as follows: Add 0.5 g to 1 g of ammonium

bromide to the hydrochloric acid solution of the phosphorus and boil gently to a volume of 5 to 10 ml, making sure the solution does not go to dryness, which will cause low results.

Dilute the solution to 50 ml, if necessary, add 0.2 g of citric acid and 2 to 3 ml of the acid magnesia mixture, cool in ice water, and stir in filtered ammonia till the solution is faintly alkaline. Finally, add 5 ml of the ammonia, stir 5 minutes or longer, and let the solution stand in a cool place for at least 4 hours.

Filter the solution through a close paper, scrub and rinse the beaker and wash the filter thoroughly with dilute ammonia (1:20), and ignite the precipitate at a temperature no higher than is necessary to burn the paper. When all the carbon has been burned and the precipitate is white, ignite at 1000° C to 1100° C to constant weight.

As the precipitate may contain silica collected from the glassware, dissolve it in 5 ml of dilute nitric acid (1:1) and dilute to 20 ml. If a residue remains, filter it off, wash with water, ignite, and weigh. Add a drop of dilute sulphuric acid, treat with hydrofluoric acid, evaporate, ignite, and reweigh. Subtract any loss in weight from the weight of the impure magnesium pyrophosphate.

Multiply the weight of the purified magnesium pyrophosphate by 27.861 and divide by the weight of sample used to find the per cent phosphorus.

### Special Solutions Required

The 2-per cent nitric acid, 2.5-per cent potassium permanganate, 1-per cent potassium nitrate, 5-per cent ammonium nitrate, 10-per cent sodium hydroxide, and dilute ammonia (1:20) solutions are readily prepared by dissolving in or mixing with water in the proportions indicated by the percentages given.

#### Acid Ammonium Molybdate Solution

Molybdic Acid (85-per cent) .....	65 g*
Ammonia (sp. gr. 0.90) .....	143 ml
Nitric Acid (sp. gr. 1.20) .....	715 ml
Water .....	142 ml

\* If pure molybdic acid is at hand, use 56 g.

Add the molybdic acid to the water and dissolve by adding the ammonia and stirring. Cool the solution and pour very slowly into the acid, the latter being constantly agitated during the addition. Add 1 or 2 drops of a 10-per cent solution of ammonium phosphate and allow the solution to stand 12 hours. Decant the clear liquid or filter through an asbestos pad as required for use.

Some chemists prefer to use neutral or nearly neutral solutions of ammonium molybdate as recommended by C. M. Johnson and A. S. T. M. methods (E-3-36T).

**Ammonium Molybdate (A. S. T. M. Formula).**—Place in an 800-ml beaker 65 g of C. P. ammonium molybdate crystals,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , 225 g of  $\text{NH}_4\text{NO}_3$ , 15 ml of  $\text{NH}_4\text{OH}$  (sp. gr. 0.90), and 600 ml of water. Stir and heat gently. When the crystals have dissolved, filter (without washing), and dilute to 1000 ml with water. This solution, however, requires more acid in the solution containing the phosphorus than is necessary when the acid reagents given above are used.

**Johnson's Formula.**—Into each of four 800-ml casseroles weigh 55 g of ammonium molybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , and 50 g of ammonium nitrate and add 40 ml of ammonium hydroxide (sp. gr. 0.95). Dilute each to 700 ml with water and heat for 30 minutes, stirring occasionally until all salts are in solution. Combine the 4 solutions, dilute to 4 liters and let stand overnight. Filter but do not wash. The solution should remain clear indefinitely.

**Dilute Nitric Acid (sp. gr. 1.20)**

Nitric Acid (sp. gr. 1.42) .....	393 ml
Water .....	620 ml

**Standard Sodium Hydroxide Solution**

Sodium Hydroxide (C.P.) .....	6.6 g
Water ( $\text{CO}_2$ -free) .....	1000 ml

**Standard Nitric Acid Solution**

Nitric Acid (sp. gr. 1.42) .....	7 ml
Water ( $\text{CO}_2$ -free) .....	1000 ml

Dissolve the sodium hydroxide in a part of the water contained in a 1-liter graduated flask. Add one ml of a saturated solution of barium hydroxide, dilute to the mark, mix thoroughly, and let stand 24 hours. Titrate against the acid, using  $\text{CO}_2$ -free water and phenolphthalein as indicator. With a pipette, transfer some of the solution to a burette and standardize against a standard steel. Adjust the volume so that 1 ml equals 0.01 per cent phosphorus on 2 g of sample or as desired, filter rapidly through a dry filter, and retain in a bottle protected with a  $\text{CO}_2$  trap of ascarite or solid KOH.

The sodium hydroxide may also be standardized accurately or approximately against Bureau of Standards standard sample of acid potassium phthalate on the basis of 1 ml equals 0.0302718 g of the phthalate. Assuming that 23 molecules of NaOH are equivalent to 1 atom of phosphorus in titrating, the normality of the NaOH solution is 0.14829. If the phosphorus is precipitated at a temperature near  $80^\circ\text{C}$  under certain conditions of acidity, the yellow precipitate apparently retains an acid radical (probably  $\text{HNO}_3$ ) which is difficult to remove by washing. If this precipitate is acid-washed free of iron and then just free of acid, the ratio is near 25:1 and the corresponding normality is 0.1611. The proper normality is, therefore, a matter for

each chemist to decide in accordance with his analytical practice, though the ratio 23:1 is now generally accepted as the one most nearly correct.

**Phenolphthalein Indicator Solution.**—Dissolve 0.2 g of the reagent in 100 ml of 50-per cent neutral ethyl alcohol or synthetic methanol. For this purpose, ethyl alcohol is best redistilled from CaO and NaOH and diluted with CO<sub>2</sub>-free water.

#### Acid-Magnesia Mixture

Magnesium Sulphate .....	65 g
Ammonium Sulphate .....	75 g
Water to make .....	1000 ml

or

Magnesium Chloride (MgCl <sub>2</sub> ·6H <sub>2</sub> O) .....	50 g
Ammonium Chloride (NH <sub>4</sub> Cl) .....	100 g
Water to make .....	1000 ml

Dissolve the salts in 500 ml of the water, add a slight excess of ammonia, let the solution stand 12 hours or longer, filter, make barely acid, and dilute to 1 liter, using sulphuric acid for the sulphate solution and hydrochloric acid for the chloride solution.

#### THE ACETATE METHOD

##### Application of the Method

While this method has been generally abandoned, it is given in brief outline here, because it is the only alternative to the molybdate method and may be found useful on occasion. It is designed to permit the determination of phosphorus in the presence of any combination of elements, but is tedious and requires some practice and skill.

Transfer 5 g of sample to a 600-ml beaker and dissolve with HNO<sub>3</sub> or HNO<sub>3</sub> + HCl, always adding HNO<sub>3</sub> first, and using as little HCl as possible. If the phosphorus is extremely low, use two 5-g portions.

Evaporate to dryness and bake to decompose Fe(NO<sub>3</sub>)<sub>3</sub>. Cool, add 30 ml HCl, heat, and evaporate just to dryness. Add 30 ml HCl, warm, dilute to 100 ml, filter, and wash with hot water.

The residue contains the silicon, tungsten, and any phosphates insoluble in hydrochloric acid.

Ignite the filter, moisten with 1 or 2 drops of H<sub>2</sub>SO<sub>4</sub> (1:1), add HF, and evaporate to dryness. Reserve for use later.

If much chromium is present, eliminate most of it by dissolving the sample in HClO<sub>4</sub> and proceed as directed in the last method given under *Chemical Separations*, finally adding 20 ml of HCl, warming, and diluting to 100 ml.

Heat the filtrate nearly to boiling, and add a mixture of 10 ml of acid ammonium sulphite and 20 ml of ammonia slowly and while stirring constantly. If a precipitate forms during this addition that



cannot be dissolved by stirring, add HCl drop by drop till it does dissolve. When nearly all of the sulphite solution has been added, heat the solution, add ammonia drop by drop until a slight greenish precipitate appears and remains after long stirring, then add the remainder of the sulphite solution. If a precipitate appears that will not dissolve on continued stirring, add HCl drop by drop till it does.

In the absence of much chromium, the solution now should be almost colorless and smell strongly of  $\text{SO}_2$ . If not, add more of the sulphite without ammonia until the solution smells strongly of  $\text{SO}_2$  and then add ammonia till a precipitate appears, which redissolves with the addition of 1 to 3 drops of HCl. Add 4 ml of HCl and boil while passing  $\text{CO}_2$  through the solution until it no longer smells of  $\text{SO}_2$ . Cool, add a few drops of ferric chloride, 1 or 2 drops of bromine water, and then ammonia drop by drop while stirring through green and white and reddish to green. If the reddish precipitate is not obtained, add HCl drop by drop, then 3 or 4 drops of bromine and repeat the neutralization to a permanent green precipitate. If high chromium and nickel obscure the red color, watch for an indication of the red due to ferric compounds. Add a few drops of acetic acid, which, in the absence of much chromium and nickel, will change the color of the solution to a deep red; then add 1 ml of acetic acid and dilute to 400 ml with boiling water. Boil 1 minute and filter as rapidly as possible on a 120- or 140-mm paper in a ribbed funnel, wash once with hot water, and permit the filter to drain dry.

The solution should run through the filter perfectly clear at first, but will soon become cloudy due to oxidation of ferrous iron, which has not been precipitated. The precipitate should be red in color due to excess basic acetate, and retain all the phosphorus as ferric phosphate, titanium phosphate, zirconium phosphate, chromium phosphate, etc. The precipitate will also contain arsenic, columbium, tantalum, thalium, uranium, and vanadium, if present, and a small part of the chromium and nickel. Danger of reducing some of the phosphates with consequent loss of phosphorus does not permit burning the paper in the usual manner.

Remove as much as possible of the precipitate from the paper by either of the following plans:

(a) Remove the paper from the funnel, open it on a piece of glass, remove the moist precipitate and transfer to a platinum dish with a spatula, dry it to  $150^\circ \text{C}$ , dry and burn the paper from a platinum wire, and add the ash to the dry precipitate.

(b) Remove the paper and precipitate from the funnel, open the paper upon a plate and dry to  $130^\circ \text{C}$ . Remove the dried precipitate by folding the paper and rubbing the surfaces gently against each other while holding over a piece of glazed paper. Then burn the paper and add the ash to the precipitate.

Grind the precipitate in a mortar with 3 g of sodium carbonate,

transfer to the crucible containing the residue from the silica, and fuse for 30 minutes or more. Leach the fusion with hot water and filter, washing with hot water. There is danger that the water-insoluble matter will retain some phosphorus. Therefore, dry and ignite the filter gently, grind and mix the residue with sodium carbonate, and repeat the fusion and extraction as before.

The precipitate contains the iron, titanium, zirconium, and most of any chromium that may have been carried down, while the filtrate contains all the phosphorus and arsenic and part of the vanadium in the steel, any aluminum present in the precipitate, and a trace of chromium oxidized during the fusion. If the initial precipitation was made at the lowest pH possible, the filtrate will contain all the phosphorus and arsenic and no more than traces of other elements.

To remove arsenic, acidify with HCl, add a few drops of acid ammonium sulphite solution, boil to the expulsion of  $\text{SO}_2$ , and pass  $\text{H}_2\text{S}$ . Filter, wash with water, and boil the filtrate and washings to remove  $\text{H}_2\text{S}$ . Add about 0.2 g of ferric chloride and a slight excess of ammonia; make just acid with acetic acid, boil, filter, and wash with hot water. Dissolve the precipitate with HCl, evaporate to low volume to expel the excess acid, and add 5 g of citric acid dissolved in 10 ml of water. Add 10 ml of acid magnesia mixture, making ammoniacal, and complete as described for the molybdate magnesia method.

### Special Solution Required

**Acid Ammonium Sulphite Solution.**—Place 20 or 25 g of sodium sulphite in a sulphur evolution flask, add a little water, and place the delivery tube in a tall beaker containing 20 ml of ammonia. Add dilute sulphuric acid to the flask slowly, and continue to pass the evolved  $\text{SO}_2$  into the ammonia until the neutral sulphite first formed has dissolved.

### Text Reference

1. Susano, C. D., and Barnett, J. H., Jr., *Ind. Eng. Chem. (Anal. Ed.)*, **8**, 183 (1936).

# Determination of Sulphur

## Methods for Determining Sulphur

Sulphur is determined either volumetrically or gravimetrically, the procedures for these two general methods being entirely different in every respect. The volumetric methods include three fundamentally different procedures known as the evolution method, the Johnson, or hot-tube evolution method, and sulphur by combustion in oxygen. Modifications of the latter, which is the most recent of all the methods that have been proposed, are described in the appendix under the heading of *Determination of Carbon and Sulphur by Combustion*. The method is applicable to all steels for the direct determination of sulphur except those containing selenium, which is evolved with the sulphur in the combustion as well as the evolution method. The method appears to be attaining the status of a standard procedure for some steels, at least.

The hot-tube evolution method of Johnson consists in treating the steel in a hot tube with a mixture of hydrochloric acid gas and hydrogen, collecting the evolved  $\text{H}_2\text{S}$  in the usual absorbents, and titrating with iodine or iodate. The method requires about  $1\frac{1}{2}$  hours, and has been applied chiefly in the determination of sulphur in certain ferro-alloys.

The ordinary evolution method is the one most widely used, and while it gives correct results on nearly all carbon steels, it fails on many alloy steels and occasionally on some plain-carbon steels from which all the sulphur is not evolved as  $\text{H}_2\text{S}$  on solution in a non-oxidizing acid. The method is also subject to various sources of error, which require constant attention to details. Various modifications of this method have been introduced from time to time.

The gravimetric methods depend upon solution of the sample, either in a strongly oxidizing solution or in an acid solution of a copper salt, followed by oxidation of the sulphur to sulphuric acid or sulphate, and precipitation of the sulphate ion as  $\text{BaSO}_4$  with  $\text{BaCl}_2$ . These methods are known as: (1) the nitric acid method; (2) the ether extraction method; (3) the nitric acid-sodium carbonate method; (4) the Meineke method; (5) the electrolytic extraction method; and (6) the fusion method. The last, which involves direct fusion of the sample in sodium peroxide, is seldom applied to steels, but is used occasionally in analyzing ferro-alloys. In the ether extraction method, the steel is dissolved in nitric acid plus 0.2 to 0.5 g of  $\text{KNO}_3$ ; the iron nitrate is decomposed by baking; the iron is converted to ferric

chloride by repeated evaporations with HCl and separated with ether. It must be modified for tungsten steels and steels insoluble in nitric acid. Since the ether extraction removes only the ferric iron and molybdenum, the advantages gained are merely those of precipitating the sulphate ion in a solution free of these elements. The nitric acid-sodium carbonate method is similar to the ether method, sodium carbonate being used to separate most of the iron. We have found neither this method nor the nitric acid-sodium carbonate method satisfactory.

In the electrolytic extraction method of Larrabee and Fowler, the solution is evaporated with perchloric acid, and the iron, etc., is separated by electrolyzing over a mercury cathode.<sup>1</sup> This procedure restricts the size of sample that may be used on account of the difficulty of separating large amounts of iron by electrolysis over mercury.

The two other methods, both of which are applied to steel, the Meineke method particularly to alloy steels, are described in the sections below. However, only the nitric acid method is recommended as giving results wholly satisfactory from the standpoint of accuracy.

#### VOLUMETRIC EVOLUTION METHOD

##### Ordinary Procedure in Absence of Molybdenum, Tungsten, Selenium, and Zirconium, Also High Percentages of Aluminum and Titanium

##### Application

The following procedure is applicable to plain-carbon steels and to alloy steels which are *rapidly* dissolved by HCl and evolve all their sulphur as  $H_2S$ , facts that must be ascertained experimentally. In the usual procedures, molybdenum, tungsten, selenium, and zirconium interfere. Selenium is largely evolved as  $H_2Se$  along with the  $H_2S$ , and a rough determination of both S and Se on the same sample is possible. In many steels, particularly those high in carbon, and some containing moderate proportions of certain other alloying elements, the proportion of the sulphur evolved is affected by heat treatment. Some of these steels can be made to evolve all the sulphur by annealing either the test piece or the drillings, the latter as follows:

Wrap 5 g of the drillings in an 11-cm filter paper, place in a porcelain crucible, add a layer of pure sugar charcoal, cover the crucible tightly, heat for 20 minutes at  $950^\circ$  to  $1000^\circ$  C (about  $1800^\circ$  F), cool slowly and treat as described below.

##### Procedure

Transfer 5 g of sample, free of scale or rust, which cause low results, to a sulphur flask and connect to the absorbing vessel, which

is usually a tumbler in which the titration is made or a 10-inch by 1-inch test tube. Assuming a tumbler is used, proceed as follows: To 150 ml of water in the titrating tumbler, add 10 ml of the absorbent solution and introduce 80 ml of HCl (1:1 or 2:1) free of  $\text{HNO}_3$  or other oxidizing substances through the funnel tube of the sulphur flask. Heat gently until the sample is dissolved and boil ( $\frac{1}{2}$  to 1 minute) until the gas in the flask is displaced with steam. As soon as the delivery tube becomes hot to the touch, disconnect the flask and remove it from the heat, leaving the delivery tube in the absorber

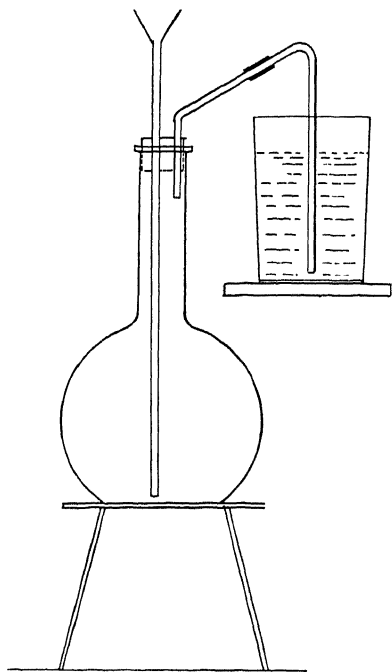


FIGURE 11. Typical apparatus for determining sulphur by the evolution method. Left: sulphur flask. Right: absorber and titrating tumbler.

and titrating tumbler. If the solution in the tumbler has become warm, repeat the determination, as a higher temperature than normal in the absorbent solution or in the solution for titrating will affect the results. Place the tumbler under the titrating burette, add 5 ml of starch solution if the solution does not contain starch and dilute HCl (1:1) to give 8 to 12 ml excess. Titrate immediately with the standard iodine or iodate solution to a permanent blue end point. The number of ml of titrating solution used, minus the blank, if theoretical titer is used, gives the sulphur in hundredths of a per cent. If the theoretical titer and a weight greater or smaller than 5 g

is used, the number of ml are divided by 100 times the weight of sample used and multiplied by 5 to find the per cent sulphur.

### Special Procedures

#### Absence of Selenium and Zirconium

As stated before, many variations of the procedure above are in use, and these are permissible if certain essential conditions are observed and kept constant for all determinations. The necessary conditions are:

(1) No oxidizing substance may be present, and the acid used must be pure and free of any trace of chlorine, nitric acid, nitrous oxides, or oxides of sulphur.

(2) The steel must be acted upon rapidly by the acid, or a slow stream of hydrogen must be kept flowing through the apparatus to carry out the  $H_2S$ .

(3) The absorbing solution must be kept alkaline during the evolution. When ammoniacal cadmium chloride is used, exposure of the sulphide to direct sunlight must be avoided, as some of the rays produce photochemical changes in the sulphide, causing low results.

(4) The temperature of the solution for titrating should not be above  $35^{\circ} C$  and is best kept at  $20^{\circ} C$  or under. Variations in room temperature have no effect.

(5) The amounts of reagents used should be the same for all titrations.

(6) The volume of the solution for titrating should be sufficiently large to hold in solution the  $H_2S$  liberated on acidifying, and always the same.

(7) The solution for titrating must be acidified before any of the titrating solution is added.

The two most important variations introduced are the following:

**The Use of Concentrated Hydrochloric Acid** has been advocated for some carbon steels and high-alloy steels. When concentrated acid is used and heat is applied to the evolution flask, a reflux condenser is required to retain the acid, as  $HCl$  gas is given off on heating to a concentration corresponding to the 1:1 acid ordinarily used. One type of condenser recommended is that known as the Pulsifier apparatus, which provides a water-cooled coil just below the outlet tube to act as a condenser and a funnel tube, through which hydrogen can be admitted following the introduction of the acid. Instead of a condenser, the usual apparatus may be used with test tube containing water between flask and absorbing vessel, with connections of glass tubing. After the absorbent is titrated, the solution in the test tube which has absorbed the  $HCl$  and some  $H_2S$  is added to the absorbent

and more of the standard iodate or iodine solution is added as necessary to obtain the correct end point. For most steels, the 1:1 acid gives the same results as the concentrated acid.

**Hydrofluoric Acid** is used to increase the speed of reaction of the hydrochloric acid with high-silicon steels, which dissolve very slowly, due to the formation of a film of silica on the surface of the cuttings. In practice, a part of the hydrochloric acid is admitted to the flask, and when the action slows down, a few ml of hydrofluoric acid are added to the remainder, which is admitted at intervals till the steel is dissolved. The exact amount of the hydrofluoric acid required depends on the per cent of silicon in the steel.

#### **Selenium Present, Molybdenum and Zirconium Absent**

No procedure has been devised to assure correct results for sulphur by the evolution method in steels containing zirconium or much molybdenum. Also, the usual procedures fail completely in the presence of selenium, a part of which is evolved as  $\text{H}_2\text{Se}$  along with the  $\text{H}_2$  and  $\text{H}_2\text{S}$ . The following method is applicable to carbon and alloy steels containing selenium, which evolves all the sulphur as  $\text{H}_2\text{S}$ , a fact that must be ascertained by experiment:

**Special Solution Required.**—*Acid Zinc-Potassium Chloride.*—Mix 10 g of zinc oxide with water and dissolve with  $\text{HCl}$ , adding but a slight excess. Then add 50 g of  $\text{KCl}$  and dilute to 1 liter. Add a solution of  $\text{KOH}$  until a small portion gives a yellow color on adding thymol blue indicator, then add dilute  $\text{HCl}$  until the color is a full red. Any other method of adjusting the pH of the solution to about 1 with the same acid and alkali is satisfactory.

**Procedure.**—Transfer 5 g of the sample to a sulphur evolution flask equipped with a funnel tube for the introduction of acid, a delivery tube, and a means of introducing hydrogen or sulphur-free natural gas. Add 60 ml of the special acid zinc-potassium chloride solution to a 10-inch by 1-inch test tube provided with a 2-hole rubber stopper carrying an inlet tube leading to the bottom and an outlet tube at the top. Connect the outlet of the evolution flask to the inlet tube, and the outlet tube to a tube leading to the bottom of a similar 10-inch by 1-inch tube containing the usual ammoniacal cadmium chloride absorbent solution used for absorbing the sulphur. Connect the evolution flask to the supply of hydrogen or natural gas, place over a heater and introduce 80 ml of dilute hydrochloric acid (1:1). Apply heat till the action is rapid, then reduce the heat till solution of the sample is complete. Increase the heat until the solution is near boiling and pass a stream of hydrogen or natural gas for 5 minutes at a rate giving a continuous flow of bubbles through the apparatus. Then disconnect the tube containing the ammoniacal cadmium chloride solution and titrate for sulphur in the usual way.

The acid zinc-potassium chloride solution retains the selenium but permits the  $\text{H}_2\text{S}$  to pass unaffected. The precipitate obtained in the ammoniacal cadmium chloride solution has a different color, an orange tint, when selenium is present from that obtained from the reaction with  $\text{H}_2\text{S}$  alone.

### Solutions required

**Dilute HCL.**—Dilute 500 ml (sp. gr. 1.19) to one liter.

**Ammoniacal Zinc Sulphate.**—Dissolve 100 g  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in 500 ml  $\text{H}_2\text{O}$  and add 500 ml  $\text{NH}_4\text{OH}$  (sp. gr. 0.90). Filter.

**Ammoniacal Cadmium Chloride.**—Dissolve 10 g  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$  in 400 ml  $\text{H}_2\text{O}$  and add 600 ml  $\text{NH}_4\text{OH}$  (sp. gr. 0.90).

Either of these solutions may be diluted to the concentration desired for absorption, and the starch solution added. Starch thus added to the ammoniacal solution causes it to yield a flocculent precipitate which dissolves more readily in dilute hydrochloric acid than a precipitate formed in the absence of starch. For use in a test tube, the solution above is diluted to 8 liters, 400 to 500 ml of the starch solution being added prior to the final dilution.

**Stock Sodium Hydroxide-Starch Solution.**—For a stock solution, mix 2 g potato starch with 10 to 20 ml of water, add to 500 ml of hot water and boil 5 minutes. When the starch solution is cold, add a solution of 92 g of sodium hydroxide in 200 ml of water and dilute to 1 liter.

For absorptions, dilute 250 ml of this stock solution to 4000 ml and use 60 ml of this solution for each determination, either full strength (when the 10-inch by 1-inch test tube is used) or diluted to the volume required for titrating, ordinarily 300 ml or 400 ml.

**Starch Solution.**—Use a fresh wheat, potato, or soluble starch. Many lots, particularly of the last, have been found unsuitable. Make 5 g into a thin paste with water and add slowly to 500 ml of boiling water. Let stand 24 hours, decant the clear solution, add 15 g KI and mix. Use within 2 or 3 days or add a preservative, usually 5 g  $\text{ZnCl}_2$  in 50 ml of water.

**Titration Solution.**—Either iodine or potassium iodate is satisfactory. However, the iodate is preferable and is generally used.

Dissolve 4 g of resublimed iodine or 1.12 g of  $\text{KIO}_3$  in a concentrated solution of 12 g of KI and dilute to 1 liter.

The resulting solution is standardized to the theoretical titer against Bureau of Standards sodium oxalate through 0.03 N  $\text{KMnO}_4$  solution and adjusted to a normality of 0.0312 so that 1 ml = 0.01 per cent sulphur on a 5-g sample. When so standardized, it is necessary to apply corrections for blank in all titrations. The titrations are carried out in the following manner.



To give a normality of 0.0312 (0.03119), 2.0897 g of sodium oxalate are dissolved in water and diluted to 1 liter.

To prepare the  $\text{KMnO}_4$  solution, 1 g of  $\text{KMnO}_4$  is dissolved in 1 liter of water, allowed to age for several days, and filtered through a pad of purified asbestos that has been thoroughly washed with water, and then alternately with some of the  $\text{KMnO}_4$  solution and water. This solution is titrated against the oxalate as follows:

Add to 80 ml of water in a 400-ml beaker, 20 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) and boil to expel traces of  $\text{SO}_2$ , etc. To make sure the solution contains no trace of reducing agents, add 1 drop of the  $\text{KMnO}_4$  solution. Dilute this solution to 300 ml with cold water, add 20 ml of the oxalate solution, and titrate to a pink end point with the  $\text{KMnO}_4$  solution, adding the latter drop by drop at first, and stirring constantly while adding the remainder. Heat the solution to  $70^\circ \text{C}$ , and continue the titration of the hot solution till 1 drop of the  $\text{KMnO}_4$  solution imparts a pink color to solution in the beaker.

The iodine or iodate solution is compared with the  $\text{KMnO}_4$  through the medium of a sodium thiosulphate solution as follows:

Dissolve 7.6 g of sodium thiosulphate in 1 liter of water.

To a 400-ml beaker add 250 ml of cold water (temperature under  $15^\circ \text{C}$ ), 20 ml of boiled dilute  $\text{H}_2\text{SO}_4$  (1:1), 10 ml of a 10-per cent solution of KI, and 20 ml of the  $\text{KMnO}_4$  solution. Stir the mixture gently and titrate the liberated iodine with the sodium thiosulphate solution until the iodine color begins to fade, then add 10 ml of plain starch solution, and continue the titration until the blue color just disappears.

Repeat these operations substituting 20 ml of the iodine or iodate solution for the  $\text{KMnO}_4$  solution.

The normality of the  $\text{KMnO}_4$  solution =  $\frac{20 \times 0.03119}{\text{number of ml of } \text{KMnO}_4 \text{ used}}$ .

The normality of the iodine or iodate solution is found by multiplying the normality of the permanganate solution by the number of milliliters of thiosulphate required by the iodine or iodate, and dividing by the number of milliliters of thiosulphate required by the permanganate.

Standardization of the solution is also made against a standard steel of the same kind and type as the steel to be analyzed, but a solution thus standardized will in most cases give slightly erroneous results on steels much lower or higher in sulphur than the standard, unless the blank is determined and corrections are properly applied. On the other hand, it has been found, through the use of the theoretical titer, that results are affected by many factors, even by the processes of manufacture. For example, slightly lower results are obtained on bessemer steel than on basic open hearth.

## GRAVIMETRIC METHODS

## Nitric Acid Method

**Caution.**—Determination of sulphur by this method must be made in a room free of sulphur fumes, and if the gas available contains sulphur, the use of electric heaters is recommended.

## Procedure for Plain-Carbon Steel

Select the coarser cuttings and transfer duplicate weights of 4.578 g each ( $33\frac{1}{3} \times 0.13734$ ) of the sample to a 400-ml tall form covered beaker or a 500-ml Erlenmeyer flask, preferably the latter. Add 50 ml  $\text{HNO}_3$  and dissolve slowly by regulating the temperature. To assure complete oxidation of the sulphur, add also 1 ml of bromine, or 1 g of NaBr, the latter in small portions. Start two blank determinations in the same way. When the cuttings have dissolved, add 0.5 g  $\text{NaNO}_3$  if NaBr was not used, and evaporate to about 10 ml. Cool, add 30 ml  $\text{HCl}$ , and evaporate just to dryness. Then add 30 ml more  $\text{HCl}$  and evaporate to the first separation of ferric chloride and redissolve with 10 ml  $\text{HCl}$ ; or expel the  $\text{HNO}_3$  by adding 30 ml of sulphur-free  $\text{HClO}_4$  (70-per cent) and evaporate to fumes, fuming 10 minutes. Dilute with 40 ml  $\text{H}_2\text{O}$  and reduce by adding an excess of sulphur-free zinc. Before the evolution of hydrogen ceases entirely, filter and wash with 75 ml of 1 per cent  $\text{HCl}$ , heat to  $70^\circ \text{C}$  and add 10 ml of a 10-per cent solution of  $\text{BaCl}_2$ . Stir in some paper pulp and let the mixture stand 24 hours. Filter through a close paper and wash the precipitate onto the filter with a solution containing 10 ml of  $\text{HCl}$  and 2 g of  $\text{BaCl}_2$  per liter. Replace the beaker containing the filtrate with a clean one, wash the filter twice with 1-per cent  $\text{HCl}$  and finally with hot  $\text{H}_2\text{O}$  until free of chlorides, thus keeping the washings separate. Cover the funnel and evaporate the washings to dryness. Take up the residue in 1 ml  $\text{HCl}$ , dilute to 25 ml, add 1 ml  $\text{BaCl}_2$ , and digest at  $80^\circ \text{C}$  for 5 or 6 hours. Filter on a close paper, wash free of chlorides with hot  $\text{H}_2\text{O}$ , and ignite both papers in a weighed platinum crucible. Add 1 drop of dilute  $\text{H}_2\text{SO}_4$  (1:1) and 1 ml  $\text{HF}$ , and evaporate to dryness. Ignite and weigh as  $\text{BaSO}_4$ . Subtract the average weight of the blanks and multiply by 3 to find the per cent sulphur.

**Procedures for Tungsten and Low-Sulphur  
Alloy Steels Insoluble in Nitric Acid**

Provide for 2 blanks and proceed as in A or B below:

(A.) Dissolve 4.578 g ( $33\frac{1}{3} \times 0.13734$ ) of sample by adding it a little at a time to a mixture of 50 ml of  $\text{HNO}_3$  and 45 ml of  $\text{HCl}$  contained in a 600-ml tall form beaker, or, better, transfer the sample to the beaker, mix the acids in another, and when the mixture has assumed a red color, add it all at once to the steel. If the action

becomes violent, set the beaker in cold water. If the steel contains tungsten, add it to the nitric acid, warm, and add the HCl a little at a time.

Evaporate the solution to about 20 ml, add 30 ml of HCl, evaporate to about 20 ml, add cautiously 2 g  $\text{Na}_2\text{CO}_3$  (omit if tungsten is present) and evaporate to dryness. Bake at  $100^\circ$  to  $105^\circ$  C about 15 minutes, cool, add 30 ml HCl and the same volume of water, and digest till soluble salts have dissolved. Filter and wash with hot dilute HCl (1:1) and hot water, and finally 3 times with hot water. Evaporate the filtrate to dryness, and bake at  $100^\circ$  C to  $105^\circ$  C. Add 10 ml HCl, warm and add 60 ml of hot water. Stir and filter immediately through a close paper into a 200-ml beaker. Wash with 1 per cent HCl and hot water till free of iron stains, and finally 5 times with cold water. Add a small amount of fine paper pulp, stir in 20 ml of 10-per cent  $\text{BaCl}_2$  solution and let stand 12 hours, or longer. Filter through a close double filter, and wash free of iron stains with a solution containing 10 ml MCl and 2 g  $\text{BaCl}_2$  per liter. Wash free of chlorides with a small jet of hot water and ignite carefully to a red heat. Cool, weigh, test for  $\text{SiO}_2$  as in *Gravimetric Methods, Nitric Acid Method, Procedure for Plain-Carbon Steel*, deduct blanks and multiply by 3 to find the per cent sulphur.

(B.) With some steels, perchloric acid, if sulphur-free, can be used to help effect solution, as follows:

Transfer the sample to a 400-ml tall form beaker, add a few crystals of sodium bromide, NaBr, and 30 ml of nitric acid,  $\text{HNO}_3$ . Heat gently, and add gradually 50 ml of tested sulphur-free perchloric acid (60 per cent  $\text{HClO}_4$ ). When the steel has dissolved, evaporate to fumes, and maintain at this temperature for 5 minutes. Cool, dilute to 75 to 100 ml, add an excess of 20-mesh sulphur-free zinc and complete the determination as directed for plain-carbon steels.

### Procedure for Tungsten Steels\*

Dissolve the sample (4.578 g) as in A above. If  $\text{HNO}_3$  alone is used, rub the cuttings with a blunt rod occasionally to remove the film of  $\text{WO}_3$  and hasten the reaction. Digest till the residue contains no dark particles, adding more acid as required, and evaporate to a point just short of dryness. Add 30 ml HCl and again evaporate. Repeat if necessary to drive off all the  $\text{HNO}_3$ . Take up in 100 ml of hot water. Filter, wash with dilute HCl (1:9), and evaporate the filtrate to dryness. Add 30 ml of HCl, and evaporate to dryness again. Add 60 ml of dilute HCl, heat gently, and dilute to 100 ml with boiling water. Add 10 ml of a solution containing 12 g of cinchonine in 100 ml of dilute HCl (1:1), stir and let stand 12 hours. Filter and wash with 3 ml of the cinchonine solution, diluted to 100 ml. Evaporate to the first appearance of a film, add 5 ml of HCl, 20 ml

\* A.S.T.M. Tentative Standard E-3 T 36. To be published, not quoted verbatim.

of  $\text{H}_2\text{O}$ , an excess of 20-mesh zinc and complete the determination as directed for carbon steel.

**Caution.**—As cinchonine may contain sulphates, it is extremely important that the same amounts be added to the blanks as to the steel. It can be tested and freed of sulphates by washing with cold water.

### Copper-Potassium Chloride or Meineke Method

This method is best suited to high-sulphur alloy steels insoluble in  $\text{HNO}_3$ , whether or not they contain selenium. The method gives low results, usually giving a recovery of about 90 per cent of the sulphur present. On this account, it is used only when no other method is applicable under the given conditions.

#### Special Solution Required

Copper-Potassium Chloride ( $2\text{KCl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ )	300 g
Hydrochloric Acid	75 ml
Water	1000 ml

Add the salt to the mixture of acid and water.

### Procedure

Start 1 blank with each sample until an average blank for each lot of chemicals is established. Add 2.748 g or 4.578 g of sample to 225 ml or 500 ml of the double chloride solution at a temperature of  $80^\circ\text{C}$  to  $90^\circ\text{C}$  and stir mechanically until the copper that separates is dissolved.

This treatment leaves an insoluble residue containing practically all of the carbon, selenium, and sulphur in the steel, and some of the iron, chromium, molybdenum, etc. Two optional methods for oxidizing the sulphur, which is present in the residue as copper sulphide, are available, namely, that of Silverman<sup>2</sup> (A) and the chlorate method (B).

(A) Filter the solution through a close rapid filter paper, and wash with hot water. Transfer the filter to a beaker, cover it with bromine water, and macerate it with a glass rod. Add 10 ml of  $\text{ZnO-HNO}_3$  mixture, previously prepared by sifting 20 g of  $\text{ZnO}$  into 100 ml of  $\text{HNO}_3$ , and 8 ml of tested sulphur-free  $\text{HClO}_4$  (70-per cent). Cover the beaker and heat, gently at first, until  $\text{HClO}_4$  is condensing on the wall of the beaker. Cool, add 100 ml of water, and boil to remove chlorine. Filter, wash, and add 10 ml of  $\text{H}_2\text{O}_2$  to reduce chromic acid. Dilute to 200 ml, boil, and precipitate the sulphates with barium chloride, completing the determination in the usual manner as directed for sulphur in carbon steel.

(B) Filter the solution through a thin close pad of thoroughly purified asbestos and wash 3 times with warm 2-per cent  $\text{HCl}$  solution. Transfer plug with residue to beaker. Add 25 ml of  $\text{H}_2\text{O}$  and 2 g of  $\text{KClO}_3$ . Then add 10 ml  $\text{HNO}_3$  and 20 ml  $\text{HCl}$  and heat to

dissolve. Filter and evaporate the filtrate just to dryness. Redissolve in 10 ml HCl, evaporate to dryness, and bake at about 110° C for twenty minutes. Dissolve the residue in 10 ml HCl and evaporate to 5 ml. Dilute to 100 ml with water, bring to the boiling point, and filter. Wash with warm water to a volume of 200 ml. To this filtrate, add 20 ml of a 10-per cent filtered solution of BaCl<sub>2</sub>. Warm for 5 minutes and let stand 6 to 9 hours. Filter and wash with a cold solution containing 10 ml HCl and 20 ml of 10-per cent BaCl<sub>2</sub> per liter. Finally, wash with hot water. Ignite and weigh as BaSO<sub>4</sub>. Subtract the blank and multiply by 5 to find the per cent sulphur for a sample of 2.748 g or by 3 for a sample of 4.578 g.

#### Text References

1. Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel," p. 234; New York, John Wiley and Sons, Inc., 1931.
2. Silverman, L., *Ind. Eng. Chem. (Anal. Ed.)*, 7, 205 (1935).

# Determination of Silicon

## Methods Available

Various methods have been proposed and used for the determination of silicon, some of those most recently proposed being colorimetric or volumetric. However, the most reliable methods are still those that involve solution of the sample in a mineral acid or a mixture of these acids, dehydration with sulphuric or perchloric acid, and final purification of the silicious residue by volatilizing the silica with hydrofluoric acid. No elements interfere seriously in these methods, though some modifications must be introduced in the presence of some, like tungsten, to avoid errors in the silicon result. The methods that follow in this section are all designed for the determination of silicon alone in one sample. In some steels, the determination of silicon is conveniently made in conjunction with the determination of certain other elements, particularly tungsten, columbium, and zirconium. Where such a combination is practicable, the treatment for the recovery of the silicon is described under the section dealing with the other element or elements sought.

## Loss from Soluble Silicon

After dehydrating and washing with acid, a certain amount of silica is found in the solution, nearly all of which can be recovered by evaporating and repeating the dehydration. The amount thus found is increased by incomplete (faulty) dehydration, and by washing with fairly concentrated solutions of hydrochloric acid, which is commonly used for this purpose. If care is exercised in these operations, practically all the silica is recovered by a second evaporation and dehydration, but a little (0.001 to 0.005 per cent) remains in solution up to the saturation point, and can be recovered only by gathering it in the bulky iron hydroxide precipitate obtained with ammonia. Since in careful work, the amount lost after one evaporation seldom exceeds 2 per cent of the total silicon present, a second evaporation is seldom made in routine work, except in the analysis of silicon steel.

## Weight of Sample

In all methods, the weight of sample is varied according to the percentage of silicon present, or the percentage of tungsten, if both are present. To avoid calculations, factor weights are used. If silicon is over 1 per cent or tungsten is high, 0.9344 g ( $2 \times .4672$ ) is generally used, when the weight of the silica in grams, divided by 2

and multiplied by 100, gives the per cent silicon. If the silicon is between 0.5 and 1.00 per cent, 2.336 g may be used and the weight of silica multiplied by 20 to find the percentage. In most steels, the silicon is under 0.5 per cent and 4.672 g are used, and the weight of silica in grams multiplied by 10 gives the per cent silicon.

### Methods Involving Dehydration of the Silica with Perchloric Acid

Two objections have been cited to the use of perchloric acid, namely, its cost is considerably greater than sulphuric acid and it frequently reacts with almost explosive violence, particularly if the carbon or the sulphur or the phosphorus is high. The last objection is overcome by treating initially with another acid, or by the use of a dilute solution of perchloric acid with or without another acid. With this precaution, the dangers from its use are those incurred in handling the chemical and in conducting the fumes out of the laboratory. Fumes of this acid with those of nitric acid and ammonia condense in hoods and form explosive mixtures. Also the fumes make wood very inflammable. This danger is largely overcome by frequent and regular cleaning of hoods.

### Procedure

Applicable to all steels except tungsten steels.

**Solution of Sample and Dehydration of the Silica.**—Transfer the sample to a 400-ml beaker of heat-resistant glass. If the sample is of an unknown steel, or if carbon, sulphur, or phosphorus is high, or for safety, add 5 to 10 ml of concentrated HCl, and add if necessary to effect solution, 5 to 10 ml of  $\text{HNO}_3$  (1:3). Warm on the hot plate until the sample is in solution, remove from the plate, and add 30 to 50 ml (according to the size of sample) of 70-per cent perchloric acid (C. P.).

Alternately, low-chromium steel will dissolve in dilute perchloric acid. For example, 35 ml of 55-per cent acid will dissolve 2.336 g of steel.

Also, stainless, heat-resistant, and similar steels low in carbon may be rapidly dissolved with a mixture composed of 17 volumes of perchloric acid (70-per cent) and 5 volumes of hydrochloric acid, but special precautions must be observed in handling the former acid to see that it is safely stored and handled only in small quantities in the laboratory. For safety, proceed in this order: weigh and transfer the sample to the beaker, mix the acids in the proportion of 9 ml to 3 ml for a sample of 1 g; 17 ml to 5 ml for a sample of 2 g; and 25 ml to 8 ml for a sample of 4 g. Add the mixture at once to the beaker and heat gently.

Cover the beaker with a watch glass, replace it upon the hot plate, and evaporate to heavy fumes of perchloric acid. Continue to heat

for 10 to 15 minutes, keeping the liquid hot enough to maintain a steady reflux of the acid on the wall of the beaker. Cool, add 100 ml  $\text{H}_2\text{O}$  and filter rapidly (suction) using paper pulp, and wash well with hot dilute  $\text{HCl}$  (2 per cent) and hot  $\text{H}_2\text{O}$ .

Ignite carefully and thoroughly, preferably in a covered crucible, as  $\text{HClO}_4$  not washed out of the silicic acid will cause popping that may result in loss of silica. Complete the determination as directed later under the heading *Purification of the Silica*, unless a referee analysis or an analysis for a special investigation requiring greater accuracy is being made, when the solution should be evaporated and the silica dehydrated a second time.

### Methods Involving Dehydration of Silicic Acid with Sulphuric Acid

#### A. Procedure Applicable to Plain-Carbon Steels

**Nitric-Sulphuric Acid Method.**—*Special Solution Required.*—Mix 667 ml of nitric acid (sp. gr. 1.20) with 333 ml of dilute sulphuric acid (1:1).

Weigh and transfer the sample (0.9344 g, 2.336 g, or 4.672 g) to a Pyrex beaker or a porcelain dish, which must be one that has not been used too often, else silica will be gathered from it. Add 20, 30, or 55 ml of the acid mixture, according to the weight of sample taken, and heat till the steel has dissolved. Evaporate until the contents of the dish are fuming strongly. Cool somewhat and add 5 ml of dilute hydrochloric acid (1:1) and 50 ml of water. Heat to boiling and filter, scrubbing the dish well with a policeman, and washing the filter free of iron with dilute hydrochloric acid (2-per cent). Transfer the filter to a platinum crucible, ignite finally at  $1000^\circ \text{C}$  or higher, cool, and weigh.

If aluminum has been added to the test piece or the steel, the silica will be contaminated with  $\text{Al}_2\text{O}_3$ . On the other hand, a small percentage of the silicon remains in solution, and a second evaporation is required to recover it. In routine work, the two errors are considered as balancing each other, an assumption that is not true for all steels, particularly low-carbon steels.

To purify the silica, following a second evaporation, or to guard against  $\text{Al}_2\text{O}_3$  contamination, moisten the residue with 2 drops of dilute  $\text{H}_2\text{SO}_4$  (1:1), add 3 to 10 ml of hydrofluoric acid (48-per cent) and evaporate slowly to dryness, preferably in an air bath, heat gradually, and finally ignite as before. Cool, weigh, and subtract the second weight from the first to find the weight of pure silica. Apply the proper factor to convert the result to per cent silicon, as given under *Weight of Sample*.



## B. Procedure Applicable to All Steels Except Those Containing Tungsten and Much Chromium

**Hydrochloric-Sulphuric Acid Method.**—*Solution of the Sample and Dehydration of the Silica.*—Transfer the sample to a 600-ml beaker of the Pyrex type, or to a 300-ml casserole or evaporating dish of porcelain or platinum. If porcelain is used, select a vessel in good condition. Dissolve the steel with an excess of HCl, if possible, adding a little  $\text{HNO}_3$  for high-nickel steels and others if necessary. When the metal has dissolved, evaporate until the solution is approaching dryness, then add 15 to 25 ml of  $\text{H}_2\text{SO}_4$ , and evaporate cautiously to prevent spitting, until copious fumes of  $\text{H}_2\text{SO}_4$  are evolved. At this stage, push the salts beneath the acid with a rod and fume for 2 or 3 minutes. Cool somewhat, add 100 ml  $\text{H}_2\text{O}$ , stir until salts are dissolved, and filter immediately through a close paper. Scrub the container thoroughly with a policeman, and wash alternately with dilute HCl (1:20) and water, until salts are dissolved, and finally 3 times with water.

In referee work, or if silicon is very high or low, evaporate the filtrate, fume, filter, and wash as before to recover soluble silica.

*Purification of the Silica.*—Transfer the filter or filters and contents to a clean, weighed platinum crucible, ignite carefully, cool, and weigh as impure  $\text{SiO}_2$ . Moisten this silica with 0.5 to 1 ml dilute  $\text{H}_2\text{SO}_4$ , add 10 to 15 ml HF, and evaporate slowly in a bath of hot air. When the contents are dry, ignite as before, cool, and weigh. The loss in weight represents pure silica, from which the per cent is obtained by multiplying by the proper factor.

## Procedure for Tungsten Steels

**Procedure A, Separating Both Silicon and Tungsten.**—Transfer 2.336 g of the sample to a 375-ml casserole (a 300-ml Pyrex beaker may be used) and add 50 ml concentrated hydrochloric acid. Cover the casserole and heat until the sample is dissolved. Remove from the hot plate and add slowly 10 ml of concentrated nitric acid. When violent action is over, cover the dish, digest till the tungstic acid is a bright yellow, and evaporate carefully to dryness. When the solution is near dryness, remove to a cooler side of the hot plate to avoid spattering, and bake to the absence of all fumes. After baking is complete, cool slightly, and add 30 ml concentrated hydrochloric acid and 20 ml of water. (If preferred, 30 ml  $\text{H}_2\text{SO}_4$  may be added, after the steel has been dissolved and treated with  $\text{HNO}_3$ . Then evaporate to fumes, cool, mix thoroughly with 5 ml HCl, and take up in 100 ml  $\text{H}_2\text{O}$ .) Heat and keep near the boiling point until all soluble salts have dissolved. Remove the dish from the hot plate, wash off the cover glass, and adjust the volume to about 100 ml with hot water. Filter on paper pulp with suction. Wash 4 times alternately with

hot dilute hydrochloric acid (1:1) and hot water and finally 4 times with hot water. In special work, evaporate the filtrate, filter, and wash as before.

Place the papers containing the tungstic and silicic acids and the impurities in a 20-ml platinum crucible and ignite at a dull red heat until the paper is gone and the residue in the crucible is yellow in color. Cool in a desiccator and weigh. Ignite again for 15 minutes at a dull red heat to insure constant weight. Volatilize silica as directed above, finally igniting at a dull red heat, not over 800° C.

**Procedure B, Separating Silicon Without Tungsten.**—Prepare a mixture of 600 ml phosphoric acid (85-per cent) and 300 ml of perchloric acid (68- to 70-per cent).

Transfer 2.336 g of sample to a 400-ml beaker, add 40 ml of the acid mixture, and heat till the steel dissolves and all black particles disappear from the residue, usually about 30 minutes. Add 30 ml of perchloric acid (68- to 70-per cent) and heat, with the beaker supported on a ring of asbestos, for 10 minutes after the acid has begun to condense on the wall of the beaker. Cool, add 100 ml of water, and stir. Filter through a close paper, wash with dilute HCl (2-per cent), and ignite gently in a platinum crucible. Weigh as slightly impure silica, moisten with 2 drops of dilute sulphuric acid (1:1), add 5 to 8 ml of hydrofluoric acid, evaporate slowly, and ignite as before. Cool, weigh, and subtract the last weight from the first to find the weight of pure silica; multiply this by 20 to find the per cent silicon.

# Determination of Copper

## Occurrence of Copper and Methods Available

Copper is added to both carbon and alloy steels to control physical properties and to increase the corrosion resistance, particularly to atmospheric corrosion. It also occurs in some iron ores and in other raw materials used in making pig iron and steel. Hence, a small percentage is likely to be found in any steel not made from carefully selected raw materials. In general, the analyst has, therefore, to deal with quantities varying from 0.005 per cent to 1.00 per cent or more.

The element is determined by several methods known as the CuS Gravimetric method, the CuS Electrolytic method, the CuS-Iodide-Thiosulphate method, the Thiosulphate-KCN method, the Colorimetric method, and the Thiocyanate-Iodate method. All give satisfactory results when properly applied and carried out, and all require a preliminary separation of the copper, either as the sulphide or the thiocyanate. These methods, with the exception of the electrolytic method, require no special equipment, and no elements interfere seriously except tungsten and molybdenum, which must be separated, the former as  $\text{H}_2\text{WO}_4$  at the beginning and the latter from the combined sulphides. Molybdenum does not interfere in the precipitation of copper by the thiocyanate method.

## Solution of Sample and Separation of Copper with Hydrogen Sulphide

### Procedure for all Steels Except Those Containing Tungsten

Transfer 1, 2, 5, or 10 g according to the copper content, to an 800-ml beaker, add 200 ml of dilute  $\text{H}_2\text{SO}_4$  (1:9), and heat gently. If much chromium or vanadium is present, add a few crystals of potassium chlorate, and boil to dissolve carbides. When solution is complete, dilute to 500 ml, heat to boiling, and saturate with  $\text{H}_2\text{S}$  for 30 minutes as the solution cools. Digest 30 minutes, add paper pulp, filter, and wash 3 times with dilute  $\text{H}_2\text{SO}_4$  (1:99) saturated with  $\text{H}_2\text{S}$ . Treat as directed under *Purification of the CuS Precipitate*.

### Procedure for Steels Containing Tungsten

Dissolve 10 g in 100 ml of dilute  $\text{HCl}$  (1:1). Add 25 ml  $\text{HNO}_3$  (1:1) a little at a time and boil gently until the precipitate of  $\text{H}_2\text{WO}_4$  is a bright yellow. Dilute to 150 ml with hot water, digest 5 minutes, filter

the solution which contains practically all of the copper, and wash with dilute HCl (1:9).

To recover copper from the  $\text{H}_2\text{WO}_4$ , dissolve it with  $\text{NH}_4\text{OH}$ , add 5 g of tartaric acid, neutralize with  $\text{H}_2\text{SO}_4$ , add an excess of 5 per cent by volume, and treat with  $\text{H}_2\text{S}$ . Filter, wash with dilute  $\text{H}_2\text{SO}_4$  (1-per cent) saturated with  $\text{H}_2\text{S}$ , and combine this precipitate with that obtained from the filtrate as directed below.

To the first filtrate, add 10 to 25 ml of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) according to proportion of chromium present, and evaporate just to fumes. Watch this evaporation carefully; if it is carried too far, insoluble basic chromic sulphate will be formed; if it is not carried far enough, nitric acid will not be completely expelled. Cool, add 100 ml of water, and, if necessary, filter and wash with dilute  $\text{H}_2\text{SO}_4$  (1:20). To the clear filtrate, add 5 g tartaric acid, neutralize with  $\text{NH}_4\text{OH}$ , add 5 per cent by volume of  $\text{H}_2\text{SO}_4$ , heat just to boiling, and pass  $\text{H}_2\text{S}$  for 15 minutes. Let the precipitate settle, then filter and wash as in the absence of tungsten.

### Solution of Sample and Separation of Copper with Sodium Thiosulphate

#### Procedure in the Absence of Tungsten

Solution of the sample may be effected in two ways, as follows:

**A. Solution in Oxidizing Mixture.**—Prepare a mixture of 667 ml of nitric acid (sp. gr. 1.20) and 333 ml of dilute sulphuric acid (1:1). Weigh and transfer the sample (1 to 10 grams) to a glazed porcelain dish, add 25 ml to 75 ml of the acid mixture, cover the dish, heat, and evaporate until the mass is fuming copiously. Cool, add 10 ml of dilute sulphuric acid (1:1) and 50 ml of hot water, and heat gently till the separated salts have dissolved. Filter and wash the filter with hot water, collecting the solution in a 600-ml beaker. Dilute to 300 to 400 ml, heat to boiling, and add sufficient (25 to 100 ml) of a 50-per cent solution of sodium thiosulphate to reduce the ferric salts. Continue to boil vigorously till the sulphides of copper, etc., have coagulated—about 5 minutes. Collect the precipitate upon an 11-cm paper, wash it free of iron salts with a 2-per cent solution of sulphuric acid saturated with  $\text{H}_2\text{S}$ , then wash it once or twice with hot water, and proceed with the purification of the sulphide and determination of copper as directed below. For many steels, further purification of the sulphide is not necessary.

**B. Solution in  $\text{H}_2\text{SO}_4$ .**—Transfer the sample to a 600-ml beaker, add 50 to 150 ml of dilute sulphuric acid (1:5), and heat till the metal has dissolved, leaving possibly some of the copper in the residue as sulphide. Dilute to 300 ml to 400 ml, heat to boiling, and precipitate the rest of the copper by adding 15 to 30 ml of a 50-per cent solution

of sodium thiosulphate, the smaller quantity being permissible, since the solution is already reduced. Continue as directed above.

### Procedure in the Presence of Tungsten

Separate the tungsten as  $\text{H}_2\text{WO}_4$  by treating as directed above under the  $\text{H}_2\text{S}$  separation of copper. Add 20 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) to the filtrate from the  $\text{H}_2\text{WO}_4$  and evaporate to fumes. Add 10 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) and 50 ml of hot water. Filter to remove silica, etc., wash the filter with water, dilute the filtrate to 300 ml, and proceed with the precipitation of the copper with thiosulphate as in the absence of tungsten.

### Purification of Copper Sulphide Precipitate—Separation of Molybdenum

Two methods are available for the separation of molybdenum.

#### A. NaOH Separation

Transfer the paper containing the copper sulphide precipitate, which may also contain the sulphides of molybdenum, vanadium, arsenic, and tin, with traces of iron, nickel, cobalt, etc., to a 30-ml tall form porcelain crucible and ignite at  $550^\circ \text{C}$ . Fuse with 2 to 4 g of an alkali-pyrosulphate. Dissolve the melt in 25 ml of dilute  $\text{HCl}$  (1:9), dilute to 100 ml, neutralize with 5-per cent  $\text{NaOH}$  solution, and add 0.3 ml in excess. Boil 3 minutes, digest 20 to 30 minutes, filter, and wash the precipitate of copper hydroxide, which may be contaminated with  $\text{Fe}$ ,  $\text{Sb}$ ,  $\text{Sn}$ , etc., with 0.5 per cent  $\text{NaOH}$  solution, and discard the filtrate or reserve for molybdenum. Dissolve the precipitate in 15 to 24 ml of hot dilute  $\text{HNO}_3$  (1:3), wash with hot water, add 5 ml  $\text{H}_2\text{SO}_4$ , and evaporate to fumes. Cool, dilute to 40 ml, add an excess of  $\text{NH}_4\text{OH}$  sufficient to hold the copper in solution, and heat to boiling. Allow the precipitate to settle, filter, and wash with hot water, or, preferably, dilute ammonia (1:4). If the precipitate is considerable in amount, repeat by dissolving in hot dilute  $\text{HNO}_3$ , and again adding  $\text{NH}_4\text{OH}$ . Neutralize the filtrate or filtrates with dilute  $\text{H}_2\text{SO}_4$  (1:1), add 4 ml in excess, and adjust the volume to 100 ml. Heat to boiling and keep the solution saturated with  $\text{H}_2\text{S}$  for 20 minutes. Filter and wash as in the absence of tungsten and molybdenum. Complete the determination by one of the methods given below under *Methods for the Determination of Copper*.

#### B. Alpha-Benzoinoxime Separation

Alternately, copper can be conveniently separated from molybdenum with alpha-benzoinoxime.<sup>1</sup>

After igniting the mixed sulphides as directed above, dissolve the residue in 10 ml of hydrochloric acid, heating and digesting till solution is complete. Transfer the solution to a 400-ml beaker, add 2 or

3 drops of nitric acid, neutralize with ammonia, and add an excess sufficient to hold copper in solution. Boil and filter, washing with a hot dilute solution (3-per cent) of ammonia. Dilute the filtrate to 250 ml, heat to boiling, and add slowly with constant stirring 10 to 15 ml of a 2-per cent solution of alpha-benzoinoxime. Boil 1 minute, add paper pulp, and filter rapidly. Wash 6 times with 3-per cent ammonia, and ignite the precipitate to CuO in a weighed porcelain or silica crucible. Complete determination as directed below.

#### METHODS FOR DETERMINATION OF COPPER

##### The Gravimetric CuO Method

After the CuS has been obtained in a pure state by any of the methods given above, or the copper separated with alpha-benzoinoxime, transfer the precipitate to a clean new porcelain or quartz crucible and ignite carefully to a final temperature of 900° C. Cool over a good desiccant and weigh as CuO. To find the per cent Cu, multiply the weight of CuO by 79.89 and divide by the weight of sample used.

##### The Electrolytic Method

Treat the sample as described above under *Purification of the Copper Sulphide Precipitate* up to the point of adding ammonia. Transfer the ammoniacal solution to a 250-ml electrolytic beaker. Neutralize with H<sub>2</sub>SO<sub>4</sub> (1:1), add an excess of 8 ml and 4 ml HNO<sub>3</sub> (1:1), weigh the cathode, and electrolyze 12 hours with 0.5 ampere. Wash the cathode with water, dip in alcohol, dry 1 minute at 100° C, and weigh. The increase in weight times 100 divided by the weight of samples gives the per cent copper.

##### The KI-Thiosulphate Volumetric Method

Three or four days before starting a determination to be completed by this method, prepare the following standard solution and standardize the day it is used, and at frequent intervals thereafter.

##### Standard Sodium Thiosulphate Solution

Dissolve 5 g of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O in 500 to 600 ml of water, add 0.1 g of Na<sub>2</sub>CO<sub>3</sub>, dilute to 1000 ml, and let the solution stand 3 or 4 days.

One ml of this solution is approximately equivalent to 0.025 per cent copper on a 5-g sample. To standardize, proceed as follows:

Transfer 0.03 to 0.05 g of pure metallic copper to a 200-ml beaker, cover the beaker, and dissolve the copper by adding 3 to 5 ml of dilute nitric acid (sp. gr. 1.20), and boiling gently to the expulsion of oxides of nitrogen. Evaporate carefully to expel most of the acid or add 3 to 5 ml of dilute H<sub>2</sub>SO<sub>4</sub> (1:1), evaporate, and fume strongly. Cool the solution, dilute with 90 ml of water, add ammonia until the color

of the solution just changes to blue, cool to room temperature, acidify with acetic acid, add 1 ml in excess, and titrate as directed in the procedure below.

### Procedure

Dissolve the ignited oxide in 5 ml  $\text{HNO}_3$ . Warm and transfer to a 200-ml beaker with 25 ml  $\text{H}_2\text{O}$ . Boil, add an excess of bromine water, and boil off. Add a slight excess of dilute  $\text{NH}_4\text{OH}$ , boil to a faint odor, add 3 ml glacial acetic acid, boil 1 minute, cool quickly, and dilute to 100 ml. Add 6 ml 50-per cent KI solution, and titrate at once with standard thiosulphate (3.9 g per liter, 3 days old, checked against a standard steel). When the brown color fades, add 3 ml fresh starch solution, and titrate to the disappearance of the blue color. Calculate the per cent copper. One ml of the sodium thiosulphate solution equals 0.001 g copper.

### The Colorimetric Method

This method is suitable for determining small percentages of copper—0.005 to 0.10 per cent with 5 g of sample. The accuracy depends upon many factors. With care and experience, the maximum error is easily held below 10 per cent.

### Procedure

Treat 5 g of sample as directed above under methods for the separation of the copper, up to and including the separation with  $\text{NaOH}$ , unless interfering elements are known to be absent, when the original sulphide precipitate may be used.

Dissolve the precipitate with a minimum quantity of dilute nitric acid (1:1), keeping the volume under 10 ml if possible. Pour the nitric acid solution into 15 ml of ammonia, adding the solution slowly and stirring constantly. Dilute the solution to 25 ml and filter through a close asbestos or frit glass filter. (Paper must not be used.) Wash with a little dilute ammonia (1:1), transfer the solution to one of two matched 100-ml Nessler tubes, and dilute to 50 ml. To the other tube, add 15 ml of ammonia, 15 ml of water, and standard copper nitrate solution from a burette until the colors match. Dilute the standard to an estimated volume less than 50 ml. To find the per cent copper, multiply the ml of standard solution used by 0.0005 times 100 and divide by the weight of sample used.

To prepare the standard solution, dissolve 0.5 g of pure copper in 25 ml of dilute nitric acid (1:1) and dilute to 1000 ml. Thus, 1 ml = 0.0005 g of copper.

### Thiocyanate-Iodate Method

Molybdenum does not interfere in this method, and one separation of the copper suffices for most steels.

**Special Solutions Required**

**Starch.**—Use a freshly prepared solution, preferably without a preservative added. (See under *Sulphur*.)

**Potassium Iodide.**—Dissolve 100 g in 100 ml of water, and test the solution for the presence of  $\text{KIO}_3$ , as described under *Standardization of Solutions*.

**Potassium Thiocyanate.**—Dissolve 50 g  $\text{KCNS}$  in 1000 ml  $\text{H}_2\text{O}$ .

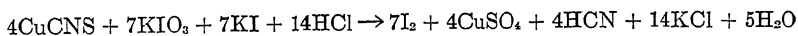
**Standard Potassium Iodate.**—Dissolve in order 20 g  $\text{KIO}_3$  and 2 g  $\text{KOH}$  in 2000 ml  $\text{H}_2\text{O}$  and standardize against standard thiosulphate. Dilute so that 1 ml is equivalent to 1 ml of the standard thiosulphate solution, which is prepared as described below.

**Standard Sodium Thiosulphate.**—Dissolve 68.75 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1000 ml  $\text{H}_2\text{O}$ . Allow the solution to age for 2 weeks, then standardize against Bureau of Standards sodium oxalate through 0.25  $N$   $\text{KMnO}_4$  solution, or against pure copper, and dilute as may be found necessary to adjust the normality of the solution to 0.2753, when 1 ml equals 0.05 per cent copper on 5 g of sample.

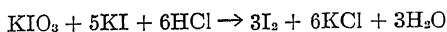
**Standardization of Solutions**

The reactions involved in titrating the copper by this method are:

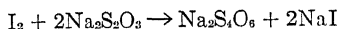
1. Reaction representing the oxidation of copper thiocyanate by potassium iodate in the presence of potassium iodide and hydrochloric acid.



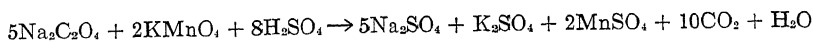
2. Reaction representing the action of  $\text{KI}$  and  $\text{HCl}$  upon the excess  $\text{KIO}_3$  added and upon all of the  $\text{KIO}_3$  used when the standard solution is titrated with sodium thiosulphate.



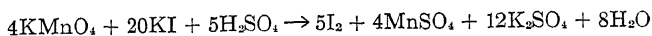
3. Fundamental reaction representing the action of sodium thiosulphate upon the iodine liberated by reactions 1 and 2, and in standardizing sodium thiosulphate solutions.



4. Fundamental reaction of sodium oxalate, potassium permanganate, and sulphuric acid in standardizing the  $\text{KMnO}_4$  solution.



5. Reaction of potassium permanganate, potassium iodide, and sulphuric acid involved in standardizing the sodium thiosulphate against the standard potassium permanganate.





6. Reactions involved when metallic copper is used as a standard

- a.  $3\text{Cu} + 8\text{HNO}_3 \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$ —Solution of the copper.
- b.  $\text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 2\text{HNO}_3$ —Expulsion of  $\text{HNO}_3$ .
- c.  $2\text{CuSO}_4 + 4\text{KI} \rightarrow \text{I}_2 + \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4$ —Direct titration of copper.
- d.  $\text{CuSO}_4 + 2\text{KCNS} \rightarrow \text{CuCNS} + \text{K}_2\text{SO}_4$ —Reaction of cupric salts with potassium thiocyanate in dilute acid solution.

From reaction 2, it is apparent that the total oxidizing power of  $\text{KIO}_3$  is equivalent to 42 atoms of iodine, and reaction 1 shows that only 14 atoms of iodine are liberated in the reaction with  $4\text{CuCNS}$ . Therefore, the equivalent of 28 atoms of I, or  $\frac{2}{3}$  of the total oxidizing power of the iodate, is used in oxidizing 4 Cu atoms of copper, and 1 liter of a normal solution of iodate equals 9.0814 (4/28 or 1/7 of 63.57) g of copper. Also, for 1 ml of the iodate solution to equal 0.05 per cent copper on a sample of 5 g, or 0.0025 g of copper, the normality of the iodate must be 0.2753. Again, provided the iodate and thiosulphate solutions are equivalent, it is evident that if, in making a titration of the copper, the thiosulphate used does not exceed  $\frac{2}{3}$  of the iodate added, a proper excess of iodate has not been added to cause reaction 1 to go to completion.

Finally, the relatively large amounts of potassium iodide taking part in the reactions, and the fact that the amounts used in determinations differ from the amounts used in standardizing the solutions, make it imperative that the KI be free of  $\text{KIO}_3$ . If the KI contains  $\text{KIO}_3$  and exactly the same amounts are used for the liberation of iodine with permanganate and with iodate, the titration being made with the same thiosulphate solution in the manner described below, the iodate will be equivalent to the permanganate, but the thiosulphate will be too concentrated by an amount equivalent to the iodate in the iodide. The reagent can be readily tested by conducting a blank test in the manner directed below with the  $\text{KMnO}_4$  or  $\text{KIO}_3$  omitted. As the  $\text{KIO}_3$  is never uniformly distributed in the KI, the use of a solution made up from a large quantity of the KI is recommended. Blank determinations may be made upon 20-ml portions of the solution, and the iodate value per ml established.

The permanganate solution of correct normality (0.2 or 0.1 N may be used) is prepared and standardized against a 0.2 N solution of sodium oxalate as described under the *Determination of Sulphur, Evolution Method, Theoretical Titer*. Directions also accompany each portion of the standard samples which are issued by the Bureau of Standards.

To standardize the sodium thiosulphate and iodate solutions against permanganate proceed as follows:

To 300 ml of water in a 600-ml beaker, add 25 ml of the  $\text{KMnO}_4$  solution from a burette and 20 ml of the 10-per cent solution of KI. While stirring the solution, add 10 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) which

has been boiled to expel  $\text{SO}_3$  or other reducing substances, and titrate most of the liberated iodine immediately with the thiosulphate solution, stirring very gently during this addition. When the color due to iodine begins to fade, add 5 ml of fresh starch solution, and continue the titration until the blue color is bleached. Repeat the titration and divide 20 times the normality of the  $\text{KMnO}_4$  solution by the average of the two results to find the normality of the sodium thiosulphate. Dilute the latter to give the normality desired, and check the normality of the adjusted solution by titrating it against 2 more portions of the permanganate.

Standardize the iodate solution by substituting it for the permanganate and titrating the liberated iodine in the same manner. Subtract 25 from the average number of ml of thiosulphate solution used, multiply the difference by the volume of the iodate solution remaining, and divide by 25 to find the number of ml of water to add to make it equivalent to an equal volume of the sodium thiosulphate solution. Dilute the solution accordingly and repeat the titration as before.

To standardize the thiosulphate solution against copper the procedure given under the KI-Thiosulphate method may be used, and a standard copper solution may be prepared by proceeding as indicated by reactions 6a and 6b. However, this method involves the use of a conversion factor to find the copper value of the solution for the thiocyanate-iodate method, and since the conditions of the titration are different, this method is not recommended. Nevertheless, such a solution may be used to check the procedure as a whole, a measured amount of the standard solution being added to the acid solution of a sample of copper-free iron or steel, which is then analyzed by the method as directed.

### Weight of Sample

If the steel contains less than 1 per cent copper, use 5 g of sample. For more than 1 per cent copper, use 2.5 g of the sample to be analyzed and 2.5 g of a standard steel that is free of copper.

### Procedure

Transfer the sample to a 750-ml flask or a 375-ml casserole.

**Carbon and Low-Alloy Steels.**—Dissolve the sample in 60 ml of  $\text{H}_2\text{SO}_4\text{-HNO}_3$  mixture [333 ml  $\text{H}_2\text{SO}_4$  (1:1) and 666 ml 1.20 sp. gr.  $\text{HNO}_3$ ], or 75 ml  $\text{H}_2\text{SO}_4$  (1:10), hot. If the mixture is used, dissolve the sample in a covered casserole, evaporate to fumes, take up in 5 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1), and dilute to 400 ml. If  $\text{H}_2\text{SO}_4$  alone is used, dilute to 300 ml, add  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  till  $\text{MnO}_2$  precipitates, and boil 15 minutes. Reduce the solution by adding 70 ml of a 25-per cent sodium sulphite solution.

**High-Chromium Nickel Steels.**—Dissolve in 50 ml of a mixture of  $\text{HCl}$  and  $\text{HNO}_3$  (equal parts), add 20 ml  $\text{HClO}_4$  (68- to 70-per cent)

and 2 ml HF, evaporate and fume 10 minutes under cover. Cool, dilute to 100 ml, boil 1 minute, filter, and wash with hot  $\text{H}_2\text{O}$ . Add  $\text{NH}_4\text{OH}$  until  $\text{Fe}(\text{OH})_3$  persists after stirring. Add 10 ml  $\text{H}_2\text{SO}_4$  (1:1), dilute to 300 ml, heat to boiling, and reduce as in carbon and low-alloy steels.

Alternately, the steel may be dissolved in a mixture of  $\text{HCl}$  and  $\text{HClO}_4$ , the chromium eliminated by volatilizing it, as described under *Chemical Separations*, the solution diluted to 400 ml, and the ferric salts reduced as for a plain-carbon steel. However, tests by South Works Laboratory show no advantage from elimination of the chromium to compensate for the extra time required.

**Steels Containing Tungsten: Chromium Present or Absent.**—Transfer 5 g of the sample to a 400-ml beaker and dissolve the cuttings with 50 ml  $\text{HCl}$ . Add slowly 30 ml  $\text{HNO}_3$  (1:1) and boil until tungstic acid is a bright yellow. Alternately, dissolve the sample in 50 ml of a mixture of  $\text{HCl}$  and  $\text{HNO}_3$  and heat till tungsten is thoroughly oxidized. Carefully add 50 ml of perchloric acid (68-per cent), and continue the heating until perchloric acid is condensing on the wall of the beaker. Cool somewhat and cautiously add 100 ml of water. Stir if the salts do not immediately dissolve and filter the solution into an 800-ml beaker to separate the tungstic acid. Wash the filter with hot water, dilute the solution to 500 ml with hot water, and add 10 ml of dilute sulphuric acid (1:6). Heat to boiling and add carefully 70 ml of 25-per cent solution of sodium sulphite.

*Separation and Titration of Copper.*—To the reduced solution, add 25 ml of thiocyanate solution, boil 5 minutes, and let stand 5 minutes. Filter on a close paper, wash the flask or beaker and the filter 10 times with cold 2-per cent  $\text{H}_2\text{SO}_4$ . Transfer the filter and precipitate to an 800-ml beaker and add 20 ml  $\text{HCl}$  (1:1) and 4 ml standard iodate for each 0.1 per cent copper. Macerate the paper thoroughly, dilute to 600 ml, and add 0.5 ml of the tested 10-per cent  $\text{KI}$  solution for each ml of iodate. Add the standard thiosulphate solution slowly with stirring until the iodine color fades. Add 5 ml starch solution and continue titrating till the blue color disappears. If the thiosulphate is less than  $\frac{1}{3}$  of the iodate, repeat the determination with more iodate. If the  $\text{KI}$  solution shows a blank due to iodate, add it to the iodate, and find the difference between the standard iodate and standard thiosulphate solutions added. Multiply this difference, which represents iodate required to oxidize the cuprous thiocyanate by 0.05 to find the per cent copper in the sample.

#### Text Reference

1. Kar, H. A., *Ind. Eng. Chem. (Anal. Ed.)*, 7, 193 (1935).

# Determination of Nickel

## Occurrence of Nickel

Nickel is added to steel for various purposes and in all proportions, from 0.10 per cent to 60 or 70 per cent. Its wide use in steel has led to contamination of scrap, and as it is not eliminated in steelmaking processes, the steel is likely to contain "residual nickel," unless special precautions are taken to exclude it. For some purposes, nickel, even in small proportions, is objectionable. So the analyst is required to determine nickel over a wide range from 0.01 per cent to 60 per cent or more.

## METHODS AVAILABLE

Nickel is determined volumetrically without a separation by titration with silver nitrate after treatment of the thoroughly oxidized solution with potassium iodide and potassium cyanide; gravimetrically or volumetrically after precipitation with the selective reagent dimethyl glyoxime; or electrolytically, following preliminary treatments to separate it from copper, chromium, molybdenum, arsenic, vanadium, and cobalt. The use of the first, commonly known as the cyanide method, is generally employed for routine and control work, while the second, or dimethyl glyoxime method, is widely used, both in routine work and in all referee or umpire analyses. In the latter, the nickel-dimethyl glyoxime precipitate may be weighed direct, or ignited to the oxide and weighed as such, or dissolved and titrated with cyanide, or treated electrically to obtain the nickel in elemental form for weighing. The relative accuracy of the four methods depends upon the percentage of nickel present and other factors. Both the cyanide and the dimethyl glyoxime methods must be varied for small and large proportions of nickel and to provide for the presence of interfering elements, as indicated later.

Special methods for determining small percentages of nickel are given under the dimethyl glyoxime method.

## Silver Nitrate-Potassium Cyanide Titration Method

### Application of the Method

In this method, the amount of nickel present must be controlled and kept within certain limits, which, with known materials, can be done by varying the weight of sample used. For analyzing both very high and very low nickel, 2 sets of standard titrating solutions are desirable. Copper, cobalt, ferrous iron, and tungsten interfere; the first, second,

and third by reacting with the cyanide, and the fourth by affecting the turbidity of the solution. Hence, provision must be made for separating these elements, if present, prior to titrating the nickel. Solutions required and the method for standardizing the titrating solutions are given at the end of this section, following which a special adaptation of the method to stainless steels is given.

### Weight of Sample

For nickel up to 4.00 per cent, use 1 g of sample. For high nickel (8 per cent to 12 per cent), use 0.25 g, and 0.5 g for nickel between 4 per cent and 8 per cent.

### Blanks

To correct titrations for blank and at the same time establish the silver nitrate equivalent of the potassium cyanide solution, which changes somewhat rapidly with age, a nickel-steel standard, free of interfering elements as noted above, is weighed and treated in the same manner as the sample. In routine work, it is not necessary to analyze a standard with each determination, but at least one standard per day should be carried through all steps of the analysis.

### Solution of Sample

Treatment of the sample is varied according to the composition of the steel as follows:

**Chromium Absent or Low: Copper, Cobalt, and Tungsten Absent.** Transfer the sample to a 400-ml beaker, add 20 ml of dilute nitric acid (sp. gr. 1.20), and heat gently till the steel has dissolved. Add 10 ml of a 15-per cent solution of ammonium persulphate, boil 5 minutes, and filter if necessary, washing with hot water. Cool the filtrate and washings and complete the determination as directed later under *Neutralization of the Solution and Titration of Nickel*.

**Chromium High: Copper, Cobalt, and Tungsten Absent.**—(1) Transfer the sample to a 400-ml beaker and dissolve in 20 ml of dilute sulphuric (1:3) acid, then add 5 ml of nitric acid, or more, if necessary, to dissolve carbide, and boil until brown fumes cease to be given off. Filter, wash with water, and complete as directed above under low chromium.

(2) Treat the sample in a 400-ml beaker with a mixture of 10 ml of nitric and 10 ml of hydrochloric acid, or dissolve in HCl alone and add HNO<sub>3</sub>, only if needed. Heat gently, and, when action ceases, add 25 ml of 60-per cent perchloric acid and continue the heating to fumes. Cover the beaker and increase the temperature until the color changes, indicating oxidation of the chromium, and for 5 minutes thereafter. Cool, dilute, filter, wash with water, and complete as directed under *Neutralization of the Solution and Titration of Nickel*.

(3) Dissolve the sample and eliminate chromium by volatilizing as

described under *Chemical Separations*. After volatilizing the chromium, cool the acid solution somewhat, dilute, and filter. Wash the filter with water and continue as directed under *Neutralization of the Solution and Titration of the Nickel*.

**Copper Present, Cobalt and Tungsten Absent.**—Remove the copper by one of the following methods, using the first in routine work only:

1. Transfer the sample to a 400-ml beaker, add 35 ml of dilute sulphuric acid (1:6), and when the steel has dissolved, add about 1 g of 18-gauge, pure aluminum wire, cut in pieces about 0.5 inch long, and coiled by winding on a stirring rod or other suitable form. Boil 10 minutes, filter rapidly, and wash the beaker and filter with water. Add 5 ml of nitric acid, boil to the complete expulsion of fumes, and proceed with the neutralization of the solution and the titration of the nickel as directed later.

Some nickel steels, particularly if they contain copper, leave 0.01 to 0.08 per cent nickel in the residue by this method. If copper is high, over 0.2 per cent, nickel is determined by the dimethyl glyoxime method described later.

2. Dissolve the sample and volatilize most of the chromium as chromyl chloride, as directed under *Chemical Separations*, using a minimum amount of perchloric acid. Add 10 ml of  $\text{H}_2\text{SO}_4$  and evaporate till the mixture is fuming strongly. Dilute to 100 to 150 ml, heat to boiling, reduce the ferric salts by adding aluminum wire, and pass hydrogen sulphide gas while the solution cools. Filter, wash with a 1-per cent solution of  $\text{H}_2\text{SO}_4$  saturated with  $\text{H}_2\text{S}$ , and boil off the  $\text{H}_2\text{S}$ . Add 10 ml of nitric acid, boil for 10 minutes, and complete the determination as directed below.

3. Nickel can also be determined by titration after precipitation of nickel by glyoxime and solution of the glyoxime precipitate as described later.

### Neutralization of the Solution and Titration of the Nickel

To the solution prepared by any of the methods described above, add ammonia until nearly neutral. Cool, add 50 ml of ammonium citrate-sulphate solution, and stir in ammonia until the solution assumes a greenish tint or changes the color of litmus to blue. To avoid reducing iron, cool to room temperature, dilute to 200 ml with cold water, and titrate by either of the following procedures:

### Procedure A: Determinations Based on the Ni Value of $\text{AgNO}_3$

Add 1 ml of the standard silver nitrate solution, and if no precipitate appears, add very dilute HCl solution until a slight precipitate forms, then dilute ammonia (1:1) drop by drop with constant stirring until the precipitate dissolves. Add 3 ml of concentrated ammonia, stir, and add 3 ml of a 10-per cent solution of potassium iodide. Slowly add

standard potassium cyanide solution from a burette until the solution is clear, and then add an excess of 2 ml. To detect the end point more easily, place the beaker containing the solution upon a black surface in front of an electric light enclosed in a metal shield. While stirring slowly, add the standard silver nitrate solution from a burette until a faint turbidity appears, which is taken as the end point. To find the per cent nickel, multiply the number of ml of cyanide solution used by the nickel titer of 1 ml, subtract the nickel value of the silver nitrate solution used, multiply the difference by 100, and divide by the weight of sample used.

**Example:**

Total volume of silver nitrate solution used .....	2.9 ml
Nickel value of 1 ml of the silver nitrate expressed in per cent .....	0.1
Total volume of potassium cyanide solution added .....	37.2 ml
Nickel value of the cyanide solution in per cent.....	0.101
Nickel value of total cyanide added ( $37.2 \times 0.101$ ).....	3.76
Nickel value of silver nitrate added .....	0.29
Weight of sample .....	0.25)
	<hr/> 3.47
Per cent nickel in sample .....	<hr/> 13.88

**Procedure B: Determinations Based upon Ni****Value of the KCN Solution**

After adding the ammonium citrate-sulphate solution, add a few drops of HCl or a solution of NaCl, if chlorides are not already present in the solution.

Add 1 ml of  $\text{AgNO}_3$  solution, measuring the solution accurately, and dilute  $\text{NH}_4\text{OH}$  until the solution is clear. Then, add the desired excess and continue by adding 2 ml of a 10-per cent solution of KI and titrating with KCN until the solution is just clear of precipitate, noting the ml of KCN solution required to titrate the nickel, plus the 1 ml of  $\text{AgNO}_3$ .

To find the value of the 1 ml of  $\text{AgNO}_3$  in terms of KCN, add 1 additional ml of  $\text{AgNO}_3$  solution to the solution just titrated, and continue the titration with KCN solution until the solution is just clear. The ml of KCN solution required for the latter titration are subtracted from the first KCN titration to give the ml of KCN required for the nickel present.

To determine a value for the KCN in terms of nickel, treat a standard sample of steel in the same way.

By this procedure it is not necessary to prepare  $\text{AgNO}_3$  solution of a definite strength, since its equivalent in ml is subtracted from the KCN used in the titration. This  $\text{AgNO}_3$  equivalent, or blank, is determined with each group of determinations, and also when new solutions are prepared.

**Cobalt, Tungsten, or Both Present**

**Procedure A.**—Dissolve 1 g in 25 ml of hydrochloric acid, add 25 ml of nitric acid slowly, and boil down to a low volume. Start a blank in the same way. Again add 25 ml to 30 ml of nitric acid, boil for 5 or 6 minutes, and dilute with 100 ml of water. If tungsten is present, separate the  $\text{H}_2\text{WO}_4$  by filtering the solution into a 500-ml beaker and washing with water. Add 24 g of citric acid in concentrated solution, neutralize with ammonia, and add 10 to 15 ml in excess. Heat to boiling, add 1 g of potassium chlorate, and boil 5 minutes. Cool, dilute to 300 ml, neutralize any excess ammonia with nitric acid, and add 4 drops of dilute ammonia (1:1) in excess. Precipitate the nickel with dimethyl glyoxime as described below.

**Procedure B.**—Cobalt is oxidized to the cobaltic condition in boiling ammoniacal solution whether  $\text{KClO}_3$  is present or not. If the solution is acidified, cobaltic salts are reduced to cobaltous salts. Nickel is precipitated more readily in a cobaltic than a cobaltous solution.

Dissolve 1 g in 35 ml of dilute  $\text{H}_2\text{SO}_4$  (1:6). Heat to dissolve and add 20 ml of dilute  $\text{HNO}_3$  (sp. gr. 1.20). Boil 10 minutes to oxidize the solution. Add 25 to 50 ml of  $\text{H}_2\text{O}$  and filter, if necessary. Discard the residue. To the filtrate, add 15 ml of concentrated  $\text{NH}_4\text{OH}$  to partially neutralize the acid. Stir and dissolve any precipitate formed by adding nitric acid. Cool thoroughly and add 50 ml of ammonium citrate solution. Carefully add dilute ammonia until the solution is just neutral to litmus. Dilute to 250 ml and add 10 ml of concentrated ammonia. Heat to boiling and boil strongly 12 to 15 minutes when the cobalt will be oxidized and ammonia will be expelled.

To the solution prepared by either of the procedures above, add 5 to 10 ml of dimethyl glyoxime solution (see next section) with constant stirring. Then stir in 10 ml of ammonium acetate solution (18-per cent), if the solution does not already contain this salt, and continue the stirring for 3 or 4 minutes. Heat to  $60^\circ \text{C}$  and cool in running water. Filter, scrub and rinse the beaker and then wash the precipitate with water. Discard the filtrate and place the beaker in which the nickel was precipitated under the funnel. Dissolve the precipitate on the paper with dilute nitric acid (sp. gr. 1.20) and wash the paper with water. Cover the beaker, boil 2 minutes, cool, and dilute to 100 ml. Add 5 ml of ammonium citrate-sulphate solution and neutralize with dilute ammonia.

To titrate the nickel, add 1 ml of standard silver nitrate or 5 ml of the standard dilute silver nitrate solution (concentration adjusted to high or low nickel), and dilute hydrochloric acid till a slight precipitate forms. Add dilute ammonia until the precipitate just dissolves, then 3 ml of concentrated ammonia and 3 ml of potassium iodide solution, both measured exactly. Add 25 ml of standard potassium cyanide solution and titrate with silver nitrate. Deduct the amount used in



the test from the blank and multiply by the proper factor (0.1 or 0.02, depending upon the solution used) to obtain the per cent nickel.

### Solutions Required

#### Ammonium Citrate-Sulphate Solution

Citric Acid .....	200 g
Ammonium Sulphate .....	270 g
Ammonia (sp. gr. 0.90) .....	200 ml
Water to make .....	1000 ml

The salts are dissolved in 700 ml of the water, the ammonia is added, and the mixture is diluted to 1 liter. As this solution is nearly neutral, it does not liberate heat on adding it to the solution.

#### Standard Silver Nitrate Solution: (For High Nickel)

Silver Nitrate .....	5.7894 g
Water .....	1000 ml

#### Standard Dilute Nitrate Solution: (For Low Nickel)

Silver Nitrate .....	1.1579 g
Water .....	1000 ml

#### Standard Potassium Cyanide Solution

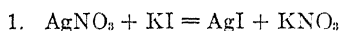
Potassium Cyanide .....	4.5 g
Potassium Hydroxide .....	1.0 g
Water .....	1000 ml

#### Standard Dilute Potassium Cyanide Solution

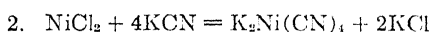
Potassium Cyanide .....	0.5 g
Water .....	1000 ml

**Standardization of Solutions.**—Each ml of the standard silver nitrate solution is equivalent to 0.1 per cent nickel and each ml of the standard dilute silver nitrate to 0.02 per cent nickel on a 1-g sample, so these solutions need no standardization. The weights are calculated from the following reactions:

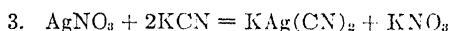
On adding KI and  $\text{AgNO}_3$



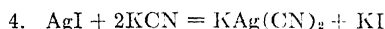
First reaction on adding KCN,



If there is an excess of silver nitrate, it also reacts with the KCN, thus,



Finally, the silver iodide is attacked giving a clear solution, thus,



If more  $\text{AgNO}_3$  is added, reaction 1 is repeated to give the end point.

The cyanide changes with age and it is made approximately equal to the silver nitrate solution. The solutions are compared at least every 8 hours or within 8 hours of using.

If this comparison is made by titrating in water with potassium iodide added without ammonium citrate and iron present, the end point is not the same as in the actual analysis. Again, if 30 ml of silver nitrate are added to a blank, followed by iodide, the heavy precipitate formed will be more difficult to dissolve with cyanide and the corrections are not the same as in the test. For these reasons, the following method of standardizing the cyanide against a standard steel is used.

A standard nickel-steel free from cobalt is treated as in a regular determination, and the number of ml of cyanide required is noted. The nickel equivalent of the silver nitrate used is added to the per cent nickel in the standard, and the sum is divided by the number of ml of cyanide to obtain the value of each ml of cyanide in terms of nickel.

**Example:**

Potassium cyanide used .....	34.1 ml
Silver nitrate used .....	3.1 ml
Nickel value of silver nitrate, $0.1 \times 3.1$ .....	0.31
Nickel in standard .....	3.15

$$\text{Total Nickel} = 3.46$$

$$\text{Nickel value per ml cyanide} = 3.46 \div 34.1 = 0.1015$$

**Notes on Special Procedures for High-Chromium Stainless and Heat-Resistant Steels Containing Much or Little Nickel and No Copper, Cobalt, or Tungsten**

Method based upon volatilization of the chromium and titration of the nickel with potassium cyanide. The following procedures were investigated without developing any advantages due to the elimination of the chromium. They are recorded here, not as standard methods, but as notes to indicate possible variations in the method and to avoid repetition of the work in the future.

**Special Solutions Required**

The silver nitrate and the dilute potassium cyanide solutions, the latter for low nickel, also the ammonium citrate-sulphate solution, are the same as those specified for the preceding method. For high nickel, the potassium cyanide solution can be made more concentrated, 7.5 g or 8 g being used with 2 g of KOH instead of 4.5 g with 1 g of KOH per liter.

The nickel values of the cyanide solutions are found by adding a solution of known nickel content to a 0.5-g sample of nickel-free iron or steel and proceeding as in a regular determination.

The nickel solution should contain approximately 2 g of nickel per liter, and may be free from nickel nitrate or treated by dissolving 2 g

of pure nickel (copper and cobalt-free) in dilute  $\text{HNO}_3$  (sp. gr. 1.20), fuming the nitrate with 20 ml of  $\text{HClO}_4$  (68- to 70-per cent), and diluting to 1 liter.

### Weight of Sample

For high nickel (over 3 per cent), use 0.5 g of sample. For low nickel, use a sample of 1 g or 2 g.

### Procedure

Transfer the weighed sample to a 500-ml Erlenmeyer flask and for a 1-g sample, add 7 ml of  $\text{HCl}$  and 35 ml of  $\text{HClO}_4$  (60-per cent). For a 0.5-g sample, the  $\text{HClO}_4$  may be decreased to 20 ml, and for a 2-g sample, the acids are increased to 10 ml of  $\text{HCl}$  and 50 ml of  $\text{HClO}_4$ . Apply gentle heat until the sample is dissolved. Evaporate rapidly, then cover and heat at the fuming temperature until the chromium is all oxidized. Now, while swirling the flask, add a small portion of  $\text{NaCl}$  (about 0.25 g) or preferably concentrated  $\text{HCl}$  (1 to 2 ml), and again heat to fuming. Repeat these operations until brown fumes of chromyl chloride cease to be given off, and 3 or 4 times after they are no longer noticeable, heating to the fuming point after the last addition.

Allow the flask to cool for 1 to 2 minutes, then rinse the wall with a jet of water and dilute to 150 ml with cold water. Add 30 to 50 ml of the ammonium citrate-sulphate solution, and while swirling, add dilute ammonia (1:1), dropwise, until the solution assumes a light green color, then add 0.5 to 1.0 ml excess. Swirl the flask, blow out the fumes, swirl again, and test by odor for ammonia. If the odor is strong or absent, add a small piece of red litmus paper, acidify and neutralize again, because too little ammonia causes high results and too much low results. Add 3 to 4 ml of a 10-per cent solution of potassium iodide and cool, if necessary, to room temperature.

From a burette, add exactly 2 ml of the standard silver nitrate solution (5.7894 g per liter for high nickel) and titrate with standard potassium cyanide solution until the cloudiness due to silver iodide is dispelled. If the end point should be overrun, add a small measured portion of the silver nitrate solution and repeat the titration. Record the total ml of the silver nitrate and of the potassium cyanide used.

To find the cyanide equivalent of 1 ml of the silver nitrate solution, add to the solution just titrated the standard solution of silver iodide till a faint opalescence appears, to produce which effect may require but a drop or two. Now add 5 ml of the cyanide solution, and titrate with the silver iodide solution to exactly the same end point as before. Divide 5, the number of ml of the potassium cyanide solution used, by the number of ml of silver nitrate used in the last titration and record the quotient as the cyanide equivalent of 1 ml of the silver nitrate solution. As this quantity is a slow changing factor for each

lot of standard potassium cyanide solution, changing but slowly from day to day, denote it by the symbol C to be determined at least once a day and for each lot of cyanide solution. The total change in this factor from the last standardization of the cyanide solution may be used to indicate when the solution should be standardized.

Alternative procedures are: (1) To back-titrate with the silver nitrate in the determination, a slight opalescence being taken as the end point. (2) To titrate in the manner described, then add the exact volume of silver nitrate used and titrate again with KCN to exactly the same end point to find the cyanide equivalent of the silver nitrate. (3) To establish at first the nickel value of the silver nitrate, which will remain constant and convert all cyanide volumes to nitrate equivalents.

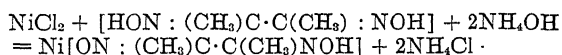
From these data, calculate the per cent nickel in the sample in accordance with the following formula:

$$\text{Per cent nickel} = \frac{(\text{ml of KCN} - \text{ml of AgNO}_3 \times C) \text{ nickel titer of KCN} \times 100}{\text{Weight of sample used}}$$

### The Dimethyl Glyoxime Method

#### Application of the Method

In this method, nickel is selectively precipitated by dimethyl glyoxime in the presence of ferric iron held in ammoniacal solution by the citric or tartaric acid, and other elements in accordance with the following reaction:



Ferrous iron tends to precipitate with the nickel, hence, the precipitate is frequently contaminated with iron. Copper, cobalt, and a high concentration of ammonia retard precipitation, the two metals contaminating the precipitate, cobalt changing the color. The precipitate is soluble in mineral acids, alcohol, and solutions of cyanides, and if the last two are excluded, it is insoluble in dilute ammonia, acetic acid, alkali acetates, and ammonium salts. If tungsten is present in proportions higher than 1 per cent, it should be separated by pretreatment with nitric acid and filtering. Small amounts of nickel are precipitated slowly, and if alcohol is present, the solution must be cold for complete precipitation. For small percentages of nickel in presence of high percentage of manganese (over 1.50 per cent), 2 precipitations are necessary to free the precipitate of iron and manganese.

#### Weight of Sample

The precipitate is bulky. Therefore, the weight of sample used is usually varied according to the nickel present as follows: For nickel

over 8 per cent, 0.25 g; for 3 per cent to 8 per cent, 0.5 g; for 1 per cent to 3 per cent, 1 g; for 0.1 to 1 per cent, 2 g; for less than 0.1 per cent, 5 g. For traces of nickel, use 10 g of sample, dissolve in HCl, oxidize with bromine, and separate most of the iron with ether.

### Procedures for Nickel and Chromium-Nickel Steels

The following procedure is written to provide correct treatment for as many different kinds of steel as possible. Procedures for residual nickel in carbon steels and high Cu-Ni-Cr alloys are given at the end of this section.

### Solutions of Dimethyl Glyoxime Required

**Ammoniacal.**—Dissolve 10 g of dimethyl glyoxime in 650 ml  $\text{NH}_4\text{OH}$  and dilute to 1 liter. Make up fresh every week. This solution is recommended where large amounts must be used, as the precipitate is slightly soluble in dilute alcohol, the solubility increasing with the temperature.

**Alcoholic.**—Dissolve 10 g in 1000 ml of ethyl alcohol (95-per cent) or pure synthetic methanol. This solution keeps indefinitely.

### Procedure

Transfer the sample to a 400-ml beaker and dissolve with 30 ml of HCl, if possible, or with dilute  $\text{H}_2\text{SO}_4$  (1:1), dilute  $\text{HNO}_3$  (sp. gr. 1.135), or mixtures of these. If  $\text{HNO}_3$  is not used initially, heat the solution almost to boiling and add 10 ml dropwise. Boil and evaporate to moist dryness. Add 30 ml HCl and boil to 15 ml. Dilute with 40 to 50 ml water and filter immediately. Wash with HCl (1:1) and hot water. If the residue is small, discard the filter and residue of silica and tungstic acid. If the residue is large, ignite, moisten with 1:1  $\text{H}_2\text{SO}_4$ , add HF, evaporate, fuse with  $\text{K}_2\text{S}_2\text{O}_7$ , dissolve melt, and add to the filtrate, unless tungsten is present, when it is best to separate it with NaOH. In the absence of cobalt, dilute to 150 ml with cold water; if cobalt is present (see also page 125), add in addition 100 ml of water for each 1 per cent of cobalt present. To avoid chance of reducing iron, add ammonia till almost neutral and cool, then add 60 ml of a cold 20-per cent solution of tartaric or citric acid, previously neutralized with ammonia, and 15 ml additional for each additional gram of sample, if more than 1 g was used. Finally, neutralize the solution with ammonia, add 1 ml excess, filter, and wash with water if a precipitate appears. Then make slightly acid with acetic acid. In the absence of cobalt, heat to 60° C and add 10 ml of the dimethyl glyoxime solution, plus 5 ml additional for each 0.01 g of nickel present. While stirring, add ammonia until slightly alkaline, and let stand for not less than 15 minutes, and preferably for 1 hour or until cold, if alcoholic dimethyl glyoxime was used. If there is little nickel present, rub the sides of the beaker with the stirring rod and let the solution

stand for several hours. In the event that cobalt or copper or both are present, add some additional dimethyl glyoxime, make the precipitation in the cold, and let stand for at least 4 hours. If the precipitate is not of the bright red color characteristic of the pure nickel salt, cobalt or much copper is indicated. In this event, dissolve it with a hot solution of 20 ml HCl (1:1) and 5 ml HNO<sub>3</sub>, wash, dilute to 300 ml, add 10 ml of tartaric or citric acid solution, and precipitate as before.

After settling, proceed by any of the following methods:

**Weighing as Nickel Dimethyl Glyoxime.**—Filter on a weighed, close, glass frit crucible filter, keeping the crucible full of liquid, and wash with hot water to which 1 drop of ammonia has been added, unless the precipitation was made with alcoholic dimethyl glyoxime, when it is best to wash with cold water. Dry at 110° C to 120° C and weigh as NiC<sub>8</sub>H<sub>14</sub>O<sub>4</sub>N<sub>4</sub>, of which 20.32 per cent is nickel. To convert the weight of nickel to per cent, multiply by 100 and divide by the weight of sample used.

**Weighing as Nickel Oxide.**—Filter through a paper, wash thoroughly as directed above, and transfer to a weighed crucible. Cover with another wet paper, heat gradually till the paper and the glyoxime are charred, and ignite to constant weight at a dull red temperature, about 800° C. Weigh as NiO, of which 78.58 per cent is nickel, multiply by 100, and divide by the weight of sample used to find the per cent nickel.

**Titration of the Nickel.**—Some chemists prefer to titrate the nickel, in which case the procedure is as follows:

Wash the beaker and red precipitate 2 or 3 times with cold water. Set aside the beaker containing the filtrate, and place the one in which the precipitation was made under the funnel. Dissolve the precipitate with dilute nitric acid (sp. gr. 1.20) and wash the paper with water. Boil 2 minutes, cool, add 5 ml of ammonium citrate-sulphate solution, dilute to 200 ml, and neutralize with ammonia.

Add 1 ml of standard silver nitrate solution or 5 ml of the dilute standard silver nitrate solution (for high or low nickel), and dilute hydrochloric acid (1:1) till a precipitate forms. Add dilute ammonia till the precipitate dissolves, then 3 ml of concentrated ammonia and 3 ml of potassium iodide solution. Add 25 ml of standard potassium cyanide solution and titrate with silver nitrate. Titrate a blank test in the same manner, and calculate the per cent nickel as directed in the preceding sections.

**Weighing as Metallic Nickel After Electrolytic Separation.**—After washing the nickel dimethyl glyoxime precipitate thoroughly, dissolve it off the paper with hot dilute nitric acid (1:3) and wash the filter thoroughly with hot water. Add 20 ml of dilute sulphuric acid (1:1)

and evaporate the solution until it is fuming strongly. Cool, add 10 ml of nitric acid, and repeat the evaporation to fumes, finally washing the cover and wall of the beaker and fuming strongly for several minutes to expel every trace of the nitric acid. Cool, cautiously add 50 ml of cold water, and heat gently till salts have dissolved. Neutralize the solution with ammonia, add an excess of 25 ml, and dilute to 170 to 180 ml. Weigh a clean platinum gauze electrode and couple it in the solution with a spiral platinum anode. Pass a D.C. current of 1 to 2 amperes for 6 to 8 hours, or until the solution is colorless. Withdraw the cathode, washing it with water while doing so, shut off the current, disconnect the cathode, dip it into water, then absolute alcohol, and dry for 15 minutes at 100° C. Weigh the cathode, subtract the original weight, multiply by 100, and divide by the weight of sample taken to find the per cent of nickel.

To check, dissolve the deposit by immersing the cathode in warm nitric acid, wash with water, dip into absolute alcohol, dry at 80° C, and weigh. The cathode is then ready for another determination.

#### **Determination of Nickel in High-Nickel, High-Copper, Chromium Steels**

In the presence of much copper, precautions must be taken to purify the nickel dimethyl glyoxime precipitate from copper. If nickel is high, as it usually is, and chromium is present, the following procedure is recommended.

**Special "Red Acid" Mixture.**—Mix concentrated hydrochloric and nitric acids in equal proportions. Allow to stand until the mixture becomes red in color before using.

Dissolve 2.5 g with 50 ml of the red acid, and add 20 ml of sulphuric acid (sp. gr. 1.84), 5 ml of perchloric acid (70-per cent), and 2 to 5 drops of hydrofluoric acid. Evaporate cautiously until nearly all the perchloric acid is expelled, cool, dilute to 100 ml, and heat to boiling. Filter and wash the filter with dilute hydrochloric acid (1-per cent), collecting the filtrate and washings in a 250-ml volumetric flask. Mix, cool to the standard temperature, dilute to the mark, mix, and remove an aliquot portion (50 ml for high nickel) with a pipette. Dilute to 150 ml, add citric or tartaric acid, neutralize with ammonia, and precipitate the nickel with dimethyl glyoxime as directed in the preceding section. Dissolve the red precipitate with a hot mixture of 20 ml HCl (1:1) and 5 ml of HNO<sub>3</sub>, wash, dilute, reprecipitate with dimethyl glyoxime, and determine nickel as directed above.

#### **Determination of Small Proportions (under 0.05 per cent) of Nickel or of Chromium and Nickel**

By the following procedures small percentages of nickel or of chromium and nickel may be determined on the same sample.

**For Nickel Only**

Use 10 g of sample and make an ether separation of most of the iron as directed under the heading of *Chemical Separations*. Avoiding open flames, evaporate the acid solution carefully until all the ether has been expelled. Add 0.2 or 0.3 g of potassium chlorate, boil till the chlorate is decomposed, dilute to 100 ml, add 3 g of tartaric or citric acid, neutralize with ammonia, filter, and wash with hot water. Add a slight excess of ammonia, stir in 10 ml of dimethyl glyoxime solution, allow to stand until the precipitate is completely formed, and complete the determination by one of the methods given in preceding sections.

**For Chromium and Nickel**

Using 10 g of sample, make an ether separation as directed under *Chemical Separations*. Avoiding open flames, evaporate the acid solution to 25 ml, cool, and add 10 ml of perchloric acid (70-per cent). Partly cover, and continue the heating until the solution fumes and for 10 minutes afterward, keeping the temperature high enough so that the perchloric acid is always condensing on the wall of the beaker. Cool quickly, add 30 ml of water, boil 5 minutes, and add 75 ml of water. Cool, add an excess of 0.04 *N* ferrous ammonium sulphate solution, and back-titrate with 0.04 *N* potassium permanganate solution.

On a 10-g sample, each ml equals 0.00695 per cent chromium. To determine nickel, add 10 ml of a 50-per cent solution of citric acid, neutralize with ammonia, add a slight excess, stir in 10 ml of dimethyl glyoxime solution, and complete the determination in the usual manner.



# Determination of Chromium

(Silicon, Vanadium, and Tungsten)

## Methods

All the methods for chromium in steel are volumetric and differ only in the reagents used to oxidize the chromium and in the details of titrating the chromic acid with a ferrous sulphate solution. Under certain conditions silicon and tungsten or vanadium, or all three, may be determined on the same sample as the chromium, though in referee or special work, results for each should be checked by another method. In all methods, the weight of sample is varied to give certain maximum and minimum weights of chromium to be oxidized, and, without exception, the same titrating solutions are employed. Therefore, directions for the preparation of these solutions are given first.

## Special Solutions Required (All Methods)

**Standard Ferrous Ammonium Sulphate—0.2 Normal; 0.1 Normal; 0.01 Normal.**—To make a 0.1 *N* solution, transfer 39.214 g  $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 6\text{H}_2\text{O}$  to a 1000-ml flask containing about 500 ml  $\text{H}_2\text{O}$ , add 100 ml dilute  $\text{H}_2\text{SO}_4$  (1:1), shake till dissolved, and dilute to 1 liter. As the solution is oxidized slowly by exposure to the air, use 40 g per liter, unless provision can be made for storing the solution under pure hydrogen or nitrogen.

This solution is best suited for titrating 30 to 100 mg of chromium. For low chromium (under 3 per cent) it is well to use half, and for high chromium (over 10 per cent) twice as much of the salt, or one-tenth as much for chromium under 0.10 per cent. The weaker solutions may be prepared by carefully diluting the 0.1 *N* solution with oxygen-free (freshly boiled) water. For example, 100 ml of the 0.1 *N* solution diluted to 1000 ml gives 0.01 *N* solution. If the solution is not stored under  $\text{H}_2$  or  $\text{N}_2$ , it should be standardized every day it is used by titrating with the standard oxidant, preferably using blanks containing all the reagents treated, as in a regular determination.

**Standard Oxidant Solutions.**—Except when the end point is obtained potentiometrically, the chromic acid is reduced by adding a slight excess of the ferrous ammonium sulphate solution, which is then back-titrated with a suitable oxidant, usually potassium permanganate. Potassium dichromate or ceric sulphate can be used in conjunction with suitable internal indicators. If the former is used, it should be purified by recrystallizing and drying at 150° C or higher and taken as the primary standard, rather than to attempt to standardize it

indirectly through permanganate against sodium oxalate. If ceric sulphate is used, it can be standardized against sodium oxalate directly by adding an excess and back-titrating with ferrous ammonium sulphate solution, using orthophenanthroline ferrous iron (2 drops of 0.025 molar solution) as indicator. However, potassium permanganate standardized against Bureau of Standards sodium oxalate is still used almost universally, and is, therefore, selected as the standard. Usually a 0.1 *N* solution is most convenient to use, though a slightly stronger solution may be employed for high chromium, and for minute percentages (under 0.01 per cent), a 0.02 *N* solution is desirable. In any case, the method of preparing the solution is the same, and will be described only for the 0.1 *N* solution.

**Standard 0.1 Normal Potassium Permanganate.**—A 0.1 *N* solution of  $\text{KMnO}_4$  requires 3.1606 g  $\text{KMnO}_4$ . In preparing the solution, however, about 3.2 g are used, as the  $\text{KMnO}_4$  is not absolutely pure and some is decomposed in making up the solution. For the same reasons, it is well to prepare a very dilute solution at the same time as the stronger solution to use in adjusting the concentration of the latter.

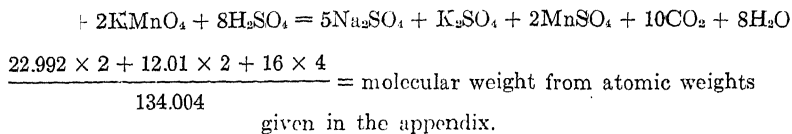
Dissolve the  $\text{KMnO}_4$  in about 900 ml of cold water and let age 1 week, or in hot water and let age 24 hours. Filter through a purified asbestos pad and dilute the stronger solution to 1 liter with the very dilute solution. Standardize against National Bureau of Standards sodium oxalate according to directions supplied with the sample, or as directed below, and adjust the concentration by adding a calculated amount of the very dilute solution. One ml of 0.1 *N* solution is equal to 0.001734 g of chromium, from which factor percentages may be calculated after proper corrections for blank, provided the chromium is all oxidized to chromic acid, or  $\text{H}_2\text{CrO}_4$ .

To avoid calculations the following table may be used:

1 ml normal solution is equivalent to	0.01734	g of Cr	
1 ml 0.5 <i>N</i> solution is equivalent to	0.00867	g of Cr	
1 ml 0.2 <i>N</i> solution is equivalent to	0.003468	g or 0.3468%	Cr on 1 g sample
1 ml 0.1 <i>N</i> solution is equivalent to	0.001734	g or 0.1734%	Cr on 1 g sample
1 ml 0.1 <i>N</i> solution is equivalent to	0.001734	g or 0.0867%	Cr on 2 g sample
1 ml 0.05 <i>N</i> solution is equivalent to	0.000867	g or 0.0867%	Cr on 1 g sample
1 ml 0.04 <i>N</i> solution is equivalent to	0.0006936	g or 0.06936%	Cr on 1 g sample
		0.03468%	Cr on 2 g sample
		0.02312%	Cr on 3 g sample
		0.01387%	Cr on 5 g sample
		0.006936%	Cr on 10 g sample
1 ml 0.02 <i>N</i> solution is equivalent to	0.0003468	g or 0.03468%	Cr on 1 g sample
		0.01734%	Cr on 2 g sample
		0.006936%	Cr on 5 g sample
		0.003468%	Cr on 10 g sample
1 ml 0.01 <i>N</i> solution is equivalent to	0.0001734	g or 0.01734%	Cr on 1 g sample
		0.00347%	Cr on 5 g sample
		0.001734%	Cr on 10 g sample
For 1 ml to be equivalent to 0.1% on	1 g sample	normality must be	0.05767
	2 g sample	normality must be	0.1154
	5 g sample	normality must be	0.2883
	10 g sample	normality must be	0.5767

### Standardization of $\text{KMnO}_4$ Solutions with National Bureau of Standards Sodium Oxalate

The reaction involved in standardizing the  $\text{KMnO}_4$  solution is:



From this reaction, it is evident that each molecule of sodium oxalate is oxidized by 1 atom of oxygen, and a normal solution of the salt, therefore, contains 67.002 g per liter, or a 0.1 *N* solution contains 6.7002 g per liter. For concentrated solutions, the salt may be dried at 100° C and portions required for titration measured by weight; for dilute solutions, a liter of solution may be prepared and carefully aliquoted by volume or by weight.

The proper weight of potassium permanganate is transferred to a volumetric flask of suitable size, dissolved in a part of the water required, diluted to the correct volume at the standard temperature of 20° C, permitted to stand for at least 3 days, and filtered through a close pad of purified asbestos.

To titrate the oxalate with the permanganate solution, transfer a proper portion of the former to a 400-ml beaker, add 100 ml of boiled dilute  $\text{H}_2\text{SO}_4$  (5 + 95) which has been previously boiled and cooled to 27° to 30° C. While stirring slowly, add from a carefully calibrated burette the potassium permanganate solution, drop by drop at first, then at the rate of 25 to 30 ml per minute until 1 drop causes the solution in the beaker to assume a pink tint. Let the beaker stand till the pink color fades, then heat the solution to 60° C, and add the permanganate solution drop by drop with constant stirring until 1 drop imparts to the solution a pink color that persists for 30 seconds. Note and record the total volume of  $\text{KMnO}_4$  solution used.

To the same volume of the specially prepared solution of sulphuric acid heated to 60° C, add the permanganate solution drop by drop till the same end point is obtained. Note and record the volume of permanganate solution required.

Subtract this blank from the total volume of solution used in the first titration to find the exact volume of permanganate required to react with the sodium oxalate. From the weight of the latter, calculate the normality of the potassium permanganate solution.

The standardization of the solutions and the analytical procedure should be checked at once by analyzing a standard sample of steel of approximately the same composition as the steels to be analyzed, particularly if the solutions are to be used for steels containing chromium in combination with vanadium or much nickel.

### Weight of Sample

In all methods, the weight of sample is varied according to the per cent of chromium likely to be present, about as follows:

For chromium under 0.05 per cent, use 10 g of sample and separate most of the iron as directed under *Chemical Separations*.

For chromium under 0.5 per cent, use 5 g of sample.

For chromium between 0.5 and 1 per cent, use 3 g of sample.

For chromium between 1 and 5 per cent, use 2 g of sample.

For chromium between 5 and 12 per cent, use 1 g of sample.

For chromium between 12 and 30 per cent, use 0.5 g of sample.

### METHODS APPLICABLE TO STEELS CONTAINING OVER 0.10 PER CENT CHROMIUM

#### Perchloric Acid Method of Oxidation

##### Tungsten Absent

**Solution of the Sample and Preparation of Same for Titration of the Chromium.**—The sample is brought into solution in various ways, as follows:

A. If the steel will dissolve at all in perchloric acid,\* transfer the sample to a 400-ml beaker (for stainless steel a 300-ml Erlenmeyer flask is preferable), and add 10 ml of water and 20 ml of perchloric acid (70-per cent), adding an additional 10 ml of the acid for each gram of sample in excess of 1 g, and 1 ml for each 10 mg of chromium present. Cover the beaker, if a beaker is used, heat gently till the sample is dissolved, then boil and heat at fuming temperature, keeping the acid condensing on the wall of the beaker or flask for 10 minutes with the condensation occurring at about half way up the wall. Grasp the beaker or flask with tongs, set momentarily upon a cold plate, then while rotating, plunge in and out of cold water several times and hold in the water 10 seconds. Add 50 to 60 ml water, boil 5 minutes, and add 5 drops of a 20-per cent solution of silver nitrate to precipitate chlorine or chlorides. Cool rapidly, dilute to 200 ml, and titrate immediately as directed later for the *Visual Titration or Potentiometric Titration of the Chromium*.

If the steel contains more than 0.020 per cent phosphorus, add 1 to 2 drops of dilute HCl (1:1) before boiling to reduce  $Mn_2O_3$  which is formed through the action of perchloric and phosphoric acids, particularly if these acids are present in certain proportions.

*\*Caution:* To avoid serious explosions, perchloric acid must be handled with great care. It should be stored on the floor in a cool place, and only small quantities handled in the laboratory. With high-carbon, high-sulphur, or high-phosphorus steels, alcohol, and other organic compounds, it reacts with explosive violence.

If desired, vanadium may be estimated by treating as directed for vanadium; and silicon, by filtering and treating in the usual way.

B. For steels attacked by nitric acid, transfer the sample to a 400-ml beaker or 300-ml flask and dissolve in 40 to 60 ml of dilute nitric acid (sp. gr. 1.20), varying the acid according to the size of the sample. Then, add 20 ml of perchloric acid (70-per cent) and 10 ml additional for each gram of steel used and 1 ml for each 10 mg of chromium, and proceed as directed above.

C. For steels not attacked by nitric acid, use HCl or a mixture of HCl (2 parts) and HNO<sub>3</sub> (1 part) with 20 ml of water to dissolve the sample. To decrease the chances of losing chromium in the next step, add 20 ml of HNO<sub>3</sub> and evaporate. Then, add perchloric acid and proceed as directed above, making sure that the fuming is continued long enough to oxidize the chromium and that conditions are controlled so that none is volatilized.

Ordinarily, oxidation of the chromium with perchloric acid alone is not complete due to the formation of Cl and H<sub>2</sub>O<sub>2</sub>. However, if the directions above are carefully carried out, oxidation of all the chromium will be complete. The quick cooling at the end with addition of silver nitrate is necessary, and it requires a little practice to perform the operation skillfully. Introduction of a chloride, or hydrochloric acid, also sulphates and sulphuric acid, into the solution after fuming with HClO<sub>4</sub> is likely to result in a loss of chromium.

**Visual Titration of Chromium and Vanadium following Oxidation with Perchloric Acid.**—The solution of chromic acid may be titrated by usual methods as given later, or by the following special method, which gives vanadium, also, if it is present. Samples of 2 g each are used for chromium up to 2 per cent. For chromium between 2 and 4 per cent, samples of 1 g each are used; for chromium over 4 per cent, 0.5-g samples are preferable.

**Special Solutions Required.**—*Ferrous Sulphate-Phosphoric Acid Mixture.*—Dissolve 10 g of ferrous sulphate crystals in 1 liter of a 15-per cent solution of orthophosphoric acid (150 ml of 85-per cent phosphoric acid in 850 ml of water). Fifty ml of this solution will reduce chromium up to 3.00 per cent on a 1-g sample, or 1.50 per cent on a 2-g sample; for higher chromium, more is required.

**Indicator Solutions.**—*Orthophenanthroline Ferrous Sulphate.*—For 0.025 M solution, dissolve 0.695 g of ferrous sulphate (FeSO<sub>4</sub> · 7H<sub>2</sub>O) in 100 ml of water, add 1.485 g of orthophenanthroline monohydrate (C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> · H<sub>2</sub>O), and stir until the latter is dissolved, giving a dark red solution.

*Orthophenanthroline Ferrous Perchlorate.*—Prepare a solution of orthophenanthroline ferrous sulphate and add, dropwise, dilute perchloric acid with constant stirring until a bright red precipitate forms and the supernatant liquid is almost colorless. The precipitate is col-

lected upon a filter, washed a few times with a small quantity of water to remove excess perchloric acid, and transferred to a suitable container. A saturated water-solution of this dye complex is used as the indicator solution, the solubility being 0.0795 g per 100 ml of water.

**Potassium Phosphate.**—Dissolve 5 pounds of dibasic potassium phosphate,  $K_2HPO_4$ , in 1100 ml of water. For 55-per cent perchloric acid, use 1 ml for each ml of the acid, or 1.3 ml for each ml of the 70-per cent acid. These proportions give a 100-per cent solution. The salt must be of C.P. grade and contain no substances that give a blank with  $KMnO_4$ .

**Standard Solutions of Potassium Permanganate.**—0.1154 *N*, 1 ml = 0.1 per cent Cr on a sample of 2 g; and 0.01154 *N*, 1 ml = 0.01 per cent Cr or 0.0294 per cent V on a sample of 2 g. These solutions are standardized against National Bureau of Standards sodium oxalate as directed under *Standard Solutions Used*.

**Procedure.**—To the solution that has been oxidized with perchloric acid and diluted to 200 ml, add a measured volume of the ferrous sulphate-phosphoric acid mixture sufficient to reduce all the chromium and vanadium present. For a blank, add the same volume of the ferrous sulphate-phosphoric acid mixture to 200 ml of water containing 20 ml of perchloric acid, and treat both solutions as follows:

Stir in 1 or 2 drops of the phenanthroline ferrous sulphate or 1 or 2 ml of the phenanthroline ferrous perchlorate indicator solution, which will color the solution red. Add 0.1154 *N* permanganate solution until the red color is bleached, leaving a faint violet color or a colorless solution. If vanadium is present the red color will return; therefore, titrate continuously and take the first fading of the red color for the end point, and let the solution stand a few minutes to test for vanadium. Record separately the ml of permanganate solution used in titrating the 2 solutions, and take the difference as the permanganate equivalent to the chromium and vanadium present.

To find the permanganate equivalent to the vanadium, if it is present, add 1 or 2 ml of the ferrous sulphate-phosphoric acid mixture to reduce the slight excess of permanganate added, and titrate as before but with the 0.01154 *N* solution. Then, record the burette reading as the zero reading for vanadium. Add 20 ml of phosphoric acid (85-per cent) and sufficient of the potassium phosphate solution to give enough potassium to react with all of the perchloric acid present (35 ml for 2 g sample dissolved with 35 ml of 55-per cent perchloric acid). If the color of the solution has changed to red, indicating the presence of vanadium, titrate to the same end point as before, and record the difference between this and the first reading as the permanganate equivalent to the vanadium.

To find the per cent chromium and the per cent vanadium, proceed as in the following example.

Ml of 0.1154 <i>N</i> permanganate to titrate the ferrous sulphate.....	18.0	
Ml of 0.1154 <i>N</i> permanganate to titrate the excess ferrous sulphate..	8.0	
Ml of 0.01154 <i>N</i> permanganate to titrate $V = 6.8$		
Ml of 0.1154 <i>N</i> permanganate equivalent to $V$ .....	0.68	
	<hr/>	
Ml of 0.1154 <i>N</i> permanganate to titrate excess ferrous sulphate over Cr .....	8.68	8.68
	<hr/>	
Ml of 0.1154 <i>N</i> permanganate equivalent to the Cr present.....		9.32
Per cent chromium = $9.32 \times 0.1$ (for 2 g sample) = 0.93		
Per cent vanadium = $6.8 \times 0.0294$ (for 2 g sample) = 0.21		

### Tungsten Present

The following method provides for the determination of both chromium and vanadium, the tungsten being held in solution by the phosphoric acid. As the steel is dissolved and these elements oxidized with a mixture of phosphoric and perchloric acids, the manganese is oxidized to  $Mn_2O_3$  and titrated with the chromium, which fact makes it necessary to apply a correction to the result for chromium. For this reason, the method is not recommended for use in work requiring the highest degree of accuracy.

**Special Solutions Required.**—*Phosphoric-Perchloric Acid Mixture.* Mix 1 vol. of perchloric acid (70-per cent, sp. gr. 1.675) with 2 vol. of phosphoric acid (85-per cent).

*Ferrous Sulphate-Perchlorate Acid Solution.*—Dissolve 15 g of ferrous sulphate ( $FeSO_4 \cdot 7H_2O$ ) in 950 ml of water and add 50 ml of perchloric acid (55-per cent).

*Potassium Phosphate Solution.*—Add 5 pounds of dibasic phosphate ( $K_2HPO_4 \cdot 3H_2O$ ) to 1100 ml of water. One ml is sufficient to react with 1 ml of 55-per cent perchloric acid, or with 0.75 ml of 70- to 72-per cent grade.

*Standard Solutions of Potassium Permanganate.*—0.1154 *N*, 1 ml = 0.1% Cr on a sample of 2 g; and 0.01154 *N*, 1 ml = 0.01% Cr or 0.0294% V on a sample of 2 g. Prepare as directed at the beginning of the chapter on chromium.

**Indicator Solution.**—A saturated solution of orthophenanthroline ferrous perchlorate.

**Procedure.**—Transfer 1 g of the sample to a 400-ml beaker, add 20 ml of the phosphoric-perchloric acid mixture, and heat gently to dissolve completely. Add 25 ml of 70-per cent perchloric acid, and heat for 20 minutes after the solution has assumed an orange color at a temperature to keep perchloric acid constantly condensing upon the wall of the beaker, which treatment should dissolve all but the silica. Now grasp the beaker with tongs, set momentarily upon a cold plate, and, while rotating, plunge it in and out of cold water a few times, and finally immerse it for 1 minute. Add 50 ml of water, boil 3 minutes, and add 5 drops of a 20-per cent solution of silver nitrate. Cool in running water, dilute to 200 ml, and titrate as follows:

With one burette filled with 0.1154 *N* and another with 0.01154 *N* permanganate solutions, prepare a blank of 100 ml of water containing 20 ml of perchloric acid (70-per cent), which is to be treated like the solution of the sample from this point on.

Add 50 ml of ferrous sulphate-perchloric acid solution and 2 ml of the indicator solution to each of the solutions to be titrated, and titrate with the 0.1154 *N* permanganate until the red color just begins to fade into green. Now place the beaker under the burette containing the more dilute permanganate solution and titrate cautiously but rapidly until the color changes to a light green or amber shade. Ignore a return of the red color and record the readings of each burette. To find the ml of the stronger solution equivalent to the weaker, divide the latter by 10.

The ml of the 0.1154 *N* permanganate used in titrating the blank, minus the ml to titrate the solution of the sample, gives the ml equivalent to the manganese, chromium, and vanadium present.

To titrate the vanadium, dilute the solution to 325 ml, add 20 ml of phosphoric acid (85-per cent) and 40 to 45 ml of the potassium phosphate solution to neutralize and precipitate the perchloric acid. Add indicator solution to a red color and titrate with the more dilute permanganate until the red color fades. Add 1 ml more of the indicator and continue the titration until the color of the solution fades into white. Multiply the ml of the permanganate used by 0.1 to convert it to ml of the 0.1154 *N* solution.

To find the percentages of chromium and vanadium in the sample, determine the manganese present and proceed as illustrated in the following example.

Ml of 0.1154 <i>N</i> permanganate used in titrating the blank . . . .			24.2
Ml of 0.1154 <i>N</i> permanganate used in 1st titration of sample . .		4.2	
Ml of 0.01154 <i>N</i> permanganate used in 2nd titration of sample . .	3.5	0.35	
Ml of 0.01154 <i>N</i> permanganate used in 3d titration of sample . .	16.5	1.65	6.2
			<hr/>
Ml of 0.1154 <i>N</i> permanganate equivalent to Cr and Mn . . . . .			18.0
Manganese in the sample, as found by another analysis	= 0.28 per cent		
Vanadium in the sample = 16.5 ml $\times$ 0.0586	= 0.97 per cent		
Chromium in the sample, if manganese is absent = 18 $\times$ 0.2	= 3.60 per cent		
Correction for manganese in the sample = 0.28 $\times$ 0.3	= 0.08 per cent		
			<hr/>

Chromium in the sample = 3.52 per cent

### Persulphate Method of Oxidation

#### Solution and Preparation of the Sample for Titration of the Chromium

The following is a standard procedure for referee and umpire analyses of chromium-bearing steels. For visual titration of the chromium in carbon and other steels containing only a small percentage of this element, a preliminary separation of most of the iron should be made,



preferably by the ether or the bicarbonate method, as directed in the section on *Chemical Separations*. If the titration is made potentiometrically, chromium as low as 0.01 per cent can be determined without a separation of the iron.

### Procedure

Transfer the sample to a 600-ml beaker and dissolve in 50 ml dilute  $\text{H}_2\text{SO}_4$  (1:4) or in 60 ml of mixed acids (160 ml  $\text{H}_2\text{SO}_4$ , 80 ml  $\text{H}_3\text{PO}_4$ , and 760 ml  $\text{H}_2\text{O}$ ). If tungsten is present and it is desired to determine chromium potentiometrically, omit the  $\text{H}_3\text{PO}_4$ . Heat till action ceases, add 5 ml  $\text{HNO}_3$ , and boil free of nitrous fumes. If carbides persist or tungsten is present, evaporate to first separation of salts, dilute with 50 ml water, add 10 ml  $\text{HNO}_3$ , and again evaporate. Add 200 ml  $\text{H}_2\text{O}$ , filter, and wash with water. To the filtrate, add 20 ml of a 1-per cent solution of  $\text{AgNO}_3$ , heat to boiling, and add slowly, while stirring, a concentrated solution of ammonium persulphate until a permanent pink color develops. If no pink color develops, add a few drops of 2-per cent  $\text{KMnO}_4$ . Boil 5 minutes, add slowly 10 ml of a 5-per cent solution of  $\text{NaCl}$  or 5 ml dilute  $\text{HCl}$  (1:1), and continue boiling until the pink or brown color disappears, adding 2 to 3 ml more  $\text{HCl}$ , if necessary. Boil 2 to 5 minutes longer, cool to room temperature, dilute to about 300 ml with cold water, and titrate as directed later for the *Visual or Potentiometric Titration of the Chromium*.

### Potassium Permanganate Method of Oxidation

#### Solution and Preparation of the Sample

Transfer the sample to a 400-ml beaker, and dissolve in 50 to 120 ml of dilute  $\text{H}_2\text{SO}_4$  (1:5). Heat gently until action ceases, oxidize by adding  $\text{HNO}_3$  dropwise, then add 20 ml excess. If tungsten is present, digest (under cover) until the tungstic acid is a light yellow color, and boil 10 minutes. If much tungsten is present, dilute to 250 ml with hot water, filter, and wash with hot water. Heat the filtrate to boiling and add, dropwise, a saturated solution of  $\text{KMnO}_4$  until the solution is a deep pink color or a permanent precipitate forms. Cover and boil 20 minutes. Filter through a close filter of purified asbestos, wash well with cold 5-per cent  $\text{H}_2\text{SO}_4$  solution, dilute to 300 ml, and titrate as directed below.

#### Visual Titration of the Chromium and Vanadium

**Procedure for Low- and Medium-Chromium Alloy Steels.**—To the cold solution obtained by any of the preceding methods, add from a burette a slight excess (2 ml or more) of standard ferrous ammonium sulphate solution. If enough is present, 1 drop will give an intense blue color when added to 1 drop of fresh  $\text{K}_3\text{Fe}(\text{CN})_6$  solution. While stirring, titrate the excess with standard potassium permanganate

solution until a faint pink end point is obtained which persists after stirring for 1 minute.

To correct the titration for dilution effect and color interference, boil the solution for 10 minutes, cool, dilute to original volume, and titrate to the same end point as before. The number of ml of  $\text{KMnO}_4$  solution used in the first titration, minus the number used in the second titration, gives the ml used in titrating the excess ferrous sulphate. This difference, subtracted from the ml of  $\text{KMnO}_4$  solution equivalent to the total ml of ferrous sulphate solution used, gives the number of ml of  $\text{KMnO}_4$  solution equivalent to the chromium present. To find the per cent chromium, multiply this quantity by 100 times the chromium factor for the permanganate, and divide by the weight of sample used.

To determine vanadium, add 5 ml  $\text{H}_3\text{PO}_4$  if not already present, and then 15 to 30 ml of 0.03 *N* ferrous ammonium sulphate or equivalent. (Test for excess as when titrating chromium, 1 ml 0.03 *N* solution = 0.0015 g V). Stir, add 8 ml of 15-per cent  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution, stir 1 minute, and titrate with 0.03 *N*  $\text{KMnO}_4$  solution to the same end point as before. Subtract the  $\text{KMnO}_4$  used from that equivalent to the ferrous sulphate used, and convert the difference to per cent vanadium.

**Alternate Procedure for High-Chromium (Stainless and Heat-Resistant) Alloy Steels.**—While it is possible to titrate high chromium with satisfactory accuracy by the method given above, the end point is made easier to detect by the use of the oxidation and reduction indicators, orthophenanthroline ferrous complex for the  $\text{FeSO}_4$ - $\text{KMnO}_4$  titration and diphenylamine sulphonic acid for  $\text{FeSO}_4$ - $\text{K}_2\text{Cr}_2\text{O}_7$  titration. With the latter indicator the chromium can, in the absence of vanadium, be titrated direct (end point a clear green) with a standard ferrous sulphate solution, which has been standardized against pure (recrystallized)  $\text{K}_2\text{Cr}_2\text{O}_7$  or a standard sample of steel.

If vanadium is present, it will be titrated with the chromium. With orthophenanthroline the end point is a clear green, and vanadium can be titrated by following a procedure similar to that given under *Visual Titration of Chromium and Vanadium Following Oxidation with Perchloric Acid*. Another procedure is given briefly as follows:

To the oxidized solution, volume 300 to 400 ml, add an excess of ferrous sulphate solution and 2 drops of a 0.025 molar orthophenanthroline indicator solution. Then titrate the excess ferrous sulphate with 0.05 *N* standard potassium permanganate solution, as indicated by the first change in color from a pink to a clear green, lasting for 30 to 60 seconds. To find the chromium, calculate as follows: From the ml equivalent to the ferrous sulphate, subtract the ml of  $\text{KMnO}_4$  used above, plus the  $\text{KMnO}_4$  used in titrating vanadium as described in the following paragraph, and multiply by the chromium factor of the  $\text{KMnO}_4$  solution.

To obtain the vanadium, which was reduced by the ferrous sulphate, add 25 grams of sodium acetate trihydrate as a buffer; heat the solution to 50° C, stirring with a thermometer, and titrate slowly to a clear green color with the 0.05 *N*  $\text{KMnO}_4$  solution. Multiply the ml of  $\text{KMnO}_4$  by the factor for vanadium and calculate to per cent.

#### Potentiometric Titration of Chromium: Absence of Vanadium and Tungsten

In this method, the chromium is titrated direct with ferrous ammonium sulphate solution, which is standardized against pure  $\text{K}_2\text{Cr}_2\text{O}_7$  by the same method of titration. Vanadium, if present, is titrated as chromium, and tungsten held in solution with  $\text{H}_3\text{PO}_4$  makes the end point hard to detect. Two types of potentiometric apparatus are available, namely, the Larrabee and the Kelly, the latter being the older and the one in more general use. With the Kelly apparatus, the solution is usually prepared by the persulphate method, and the procedure is as follows:

Place the beaker containing the solution in position, and adjust the apparatus to bring the needle or beam of light near the left end of the scale. Add the standard ferrous sulphate solution slowly until the indicator moves to the right and remains in this position. If the end point is overrun, add standard potassium dichromate solution till the indicator moves back to the left, then the ferrous sulphate solution until one drop causes the indicator to move permanently to the right. Multiply the ml of ferrous ammonium sulphate actually used in reducing the chromic acid by its chromium value times 100 and divide by the weight of sample used to find the per cent chromium.

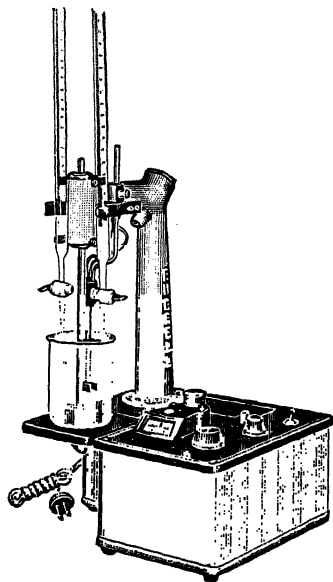
#### Titration with the Larrabee Potentiometric Apparatus

This instrument, in its latest form, is shown in the accompanying figure. The assembly includes burette and beaker supports, a stirring device, bimetallic electrodes, and a potentiometric unit. The electrodes consist of a pure gold and a pure platinum rod each with small vanes of the same metal at the bottom, and are supported to remain in correct position during titrations. To keep the electrodes in condition for accurate titrations, they are cleaned daily by immersing them in a hot saturated solution of potassium dichromate in concentrated sulphuric acid. To make a titration with this apparatus, proceed as follows:

Transfer the solution, in which manganese compounds have been reduced by boiling with  $\text{HCl}$ , to the titrating beaker, and cool it to 15° C. Place the beaker on its support so as to immerse the electrodes and stirrer in the solution to be titrated. Turn the switches starting the stirrer and connecting the potentiometric unit. Then add standard ferrous ammonium sulphate solution until 1 drop causes the indicator needle to be permanently deflected.

As the end point is approached, the potential changes, throwing the needle in a direction opposite to the final throw, and it becomes necessary to adjust the needle to the zero mark after each addition of the standard ferrous ammonium sulphate solution. At the end point, the needle will be deflected off the scale in a direction opposite to the previous trend.

FIGURE 12. View of Larrabee potentiometric apparatus with beaker and burette assembled ready for a titration. United States Patent No. 2,071,697, February 23, 1937. Courtesy, Burrell Technical Supply Company, Pittsburgh, Pennsylvania.



To find the per cent chromium in the sample, multiply the number of ml of standard ferrous ammonium sulphate added by 100 and the chromium value of 1 ml, and divide by the weight of sample used.

#### Determination of Chromium Using the Larrabee Potentiometric Apparatus

The complete procedure for determining chromium in steel with the Larrabee apparatus is briefly described as follows:

Vary the weight of sample according to the chromium present using 2 g for chromium between 0.01 and 1.00 per cent and 1 g for higher percentages. For chromium under 0.01 per cent, a larger sample, of 5 to 10 g, is required and it is then necessary to separate most of the iron by the ether or bicarbonate methods as described under *Chemical Separations*.

If possible, dissolve the sample in dilute sulphuric acid (sp. gr. 1.20, or about 1:4), using 100 ml for 2 g and 80 ml for 1 g. Evaporate the solution to a volume just short of the fuming point to avoid formation

of basic salts and oxidize the iron by adding drop by drop 4 to 5 ml of  $\text{HNO}_3$ , stirring constantly. Continue the evaporation until ferric salts begin to separate, but avoid fuming. Add 100 ml of water, stir, and filter if necessary to remove  $\text{SiO}_2$  or other insoluble matter. If there is a residue, ignite gently, volatilize the  $\text{SiO}_2$  with  $\text{HF}$ , fuse with a minimum amount of sodium carbonate, dissolve with a slight excess of  $\text{H}_2\text{SO}_4$ , and add the solution to the original filtrate.

To oxidize the chromium, dilute the solution to 200 ml, add 2 to 3 ml of a 1-per cent solution of  $\text{AgNO}_3$  and 5 to 10 ml of a 25-per cent solution of ammonium persulphate. Heat the solution to boiling and add more of the persulphate, if no color develops. Boil 8 to 10 minutes after the permanganate color appears. Add 5 ml of  $\text{HCl}$  and boil 1 to 2 minutes after all the manganese compounds appear to be reduced. Cool the solution to  $15^\circ \text{C}$  or below, then titrate and calculate the per cent chromium as directed above.

#### METHODS FOR CARBON STEELS AND OTHER STEELS CONTAINING CHROMIUM UNDER 0.10 PER CENT

For chromium under 0.10 per cent, a preliminary separation of most of the iron is desirable to obtain results of highest accuracy. The following methods have been used with satisfactory results.

##### Procedure Following an Ether Separation of Iron and Molybdenum

Use a sample of 2, 5, or 10 g, according to the accuracy desired, and separate most of the iron by dissolving and treating with ether as directed in the section on *Chemical Separations*, and continue as follows:

Evaporate the acid solution to 25 ml, then add a few drops of  $\text{HNO}_3$ , and evaporate almost to dryness to expel all the ether. Add cautiously 10 ml of perchloric acid (70-per cent) and continue the evaporation to fumes. Cover the beaker with a small rod under one edge of the cover glass, heat till the acid is condensing on the wall of the beaker, and hold at this temperature for 10 minutes. Remove the cover, cool as quickly as possible, add 30 ml of water, and boil 5 minutes to obtain a solution free of oxides of chlorine and hydrogen, which prevent complete oxidation of the chromium. Cool to room temperature, add 75 ml of cold water, and titrate as follows:

**Chromium and Nickel to be Determined.**—Add an excess of 0.04  $N$  ( $N/25$ ) ferrous ammonium sulphate solution, and titrate the excess with 0.04  $N$  potassium permanganate solution to a pink end point that persists for 1 minute, remembering that if vanadium is present the end point will be a fading one till the vanadium is oxidized. Titrate the same volume of the ferrous sulphate solution under the same conditions of volume, temperature, and acidity to the same end point. From

the ml of  $\text{KMnO}_4$  solution used in this blank titration, subtract the ml used in titrating excess added to the solution of the sample to find the ml of  $\text{KMnO}_4$  solution equivalent to the chromium present.

1 ml of 0.04 solution = 0.0347 per cent chromium on 2 g of sample  
0.0139 per cent chromium on 5 g of sample  
0.00694 per cent chromium on 10 g of sample

Time for an analysis to this point,  $1\frac{1}{2}$  to  $2\frac{1}{2}$  hours.

**To Determine Nickel, after Titrating for Chromium.**—Add 10 ml of a 50-per cent solution of citric acid, neutralize with ammonia, add a small excess, and precipitate the nickel by stirring in 10 ml of dimethyl glyoxime solution. When the precipitate has fully formed, filter, wash with cold water, and complete the determination either gravimetrically or by titrating the nickel with cyanide as directed in the methods for *Nickel*.

**Chromium, Vanadium, and Nickel can be determined on the same sample,** vanadium less accurately, by proceeding as follows:

After titrating the chromium, add 15 ml of a (1:1) solution of dibasic potassium phosphate, filter, add a few drops of sulphuric or hydrochloric acid, and sufficient ferrous sulphate to reduce vanadium and give a decided excess. Stir thoroughly, add 5 ml of a freshly prepared 15-per cent solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and continue stirring for at least 1 minute to oxidize the excess ferrous sulphate. Titrate with 0.01 *N*  $\text{KMnO}_4$  solution to a definite pink tint. If the chrome color interferes, boil, cool, and titrate to the same end point for the blank.

For nickel, boil to decompose the ammonium persulphate. Cool and proceed as directed for nickel above.

### Procedure Using the Bicarbonate Separation

Use a sample of 5 or 10 g and separate iron and manganese by the bicarbonate method as directed under *Chemical Separations*. Wash the precipitate with water containing a little bicarbonate, then dry and ignite it in an iron crucible free of nickel, chromium, or vanadium. Add 10 to 12 times its weight of sodium peroxide, mix, and fuse at a low temperature. Dissolve the melt in cold water, add 1 g of the sodium peroxide, boil 5 to 10 minutes, let the precipitate settle, and filter through glass cotton or an asbestos pad. Wash with 2-per cent  $\text{NaOH}$  containing 10 g of  $\text{Na}_2\text{SO}_4$  per liter, and determine chromium by comparing the color with a standard solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  containing  $\text{NaOH}$  in about the same concentration.

To determine chromium and vanadium by titration, acidify the solution with  $\text{H}_2\text{SO}_4$ , adding 5 ml in excess, and dilute to 200 ml. Add 10 ml of a 1-per cent solution of  $\text{AgNO}_3$ , 5 ml of a 30-per cent solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and a few drops of a 2-per cent solution of

KMnO<sub>4</sub>. Boil 5 minutes, add 10 ml of a 5-per cent solution of NaCl or 5 ml of dilute HCl (1:1), and continue to boil for 5 minutes after the pink or brown color has disappeared. Cool and titrate as directed above under *Procedure Following an Ether Separation*.

### Method Without Separating Iron, Chromium and Vanadium

**Special Ferrous Sulphate-Phosphoric Acid Mixture Required.**—Dissolve 6 g of pure ferrous sulphate crystals in 6800 ml of water and add 1200 ml of phosphoric acid (85-per cent), or dissolve 1 g of ferrous ammonium sulphate in 1 liter of a solution containing 150 ml of phosphoric acid (85-per cent).

**Standard Potassium Permanganate Solution.**—0.01154 *N*. One ml equals 0.01 per cent chromium on 2 g of sample.

**Procedure.**—Transfer 2 g to a 400-ml beaker, add 25 ml of perchloric acid (70-per cent) or 35 ml of the 55-per cent grade, cover the beaker, and heat gently until the steel is dissolved. Evaporate to fumes, and maintain the temperature to keep the acid condensing on the wall of the beaker for 10 minutes. Remove the cover, place beaker momentarily on a cold plate, and swirl with bottom in water for 10 seconds. Add 50 ml of water, boil 5 minutes, cool, add 5 drops of a 20-per cent solution of silver nitrate, and dilute to 200 ml. Prepare a blank test in the same way, and carry it through all operations that follow.

To titrate the chromium, add 50 ml of the ferrous sulphate-phosphoric acid solution, and 1 ml of phenanthroline ferrous perchlorate indicator, or more if necessary to obtain a good color. Titrate the excess ferrous sulphate rapidly to avoid low results, until the red color fades out. As a return of the red color indicates vanadium, take the first disappearance of the red as the end point.

To titrate vanadium, which is still in the quadrivalent state, add 20 ml of phosphoric acid (85-per cent) and 35 ml of dibasic phosphate solution, and titrate until the red color disappears.

Find the per cent chromium and vanadium by calculations as illustrated in the following example.

Ml of KMnO<sub>4</sub> solution required to titrate 50 ml of ferrous sulphate: 13.5

Burette Readings: first, 0.2 ml; second, 12.0 ml; third, 12.4 ml

Ml of KMnO<sub>4</sub> solution to titrate vanadium = (12.4 - 12.0) = 0.4

Vanadium in sample =  $0.4 \times 0.029 = 0.012$  per cent

Ml of KMnO<sub>4</sub> solution to titrate chromium =  $13.5 - (12.4 - 0.2) = 1.3$

Chromium in sample =  $1.3 \times 0.01 = 0.013$  per cent.

### Titration of Chromium by the Arsenite-Osmic Acid Method

**Arsenite Reduction with Osmic Acid as Catalyst.**—This method, developed in the course of our research on methods of analysis, is not

influenced by presence or absence of vanadium. Osmic acid is poisonous and costly, but little is required, and with due care it can be safely handled. The method as applied to low-chromium steels (under 1-per cent) is as follows:

*Procedure.*—To the cooled oxidized solution with a volume of about 50 ml, add 6 drops of 0.01 molar solution of osmic acid as a catalyzer, arsenite solution until the yellow color of chromium fades and shows the violet of reduced chromium. Then, add an excess of the arsenite (2 ml of 0.03 *N* or 6 ml of 0.01 *N*) and dilute the solution to 200 ml. Add 1 drop of phenanthroline ferrous sulphate complex or 1 ml of phenanthroline ferrous perchlorate, preferably the latter, then titrate with permanganate until the red color turns colorless or a very light blue. If vanadium is present, the color may return; continue the titration until the color does not return.

*Solutions Required.*—The permanganate is made preferably 0.01154 *N* and standardized against oxalate or arsenious oxide of the Bureau of Standards. The arsenite used may be the same as that used for the titration of manganese in steel (1 ml = 0.1 per cent Mn on 0.5-gram sample); if the chromium is under 0.10 per cent and accuracy of 0.001 per cent is desired, the arsenite may be one-third the concentration of the solution above.

*Blank Due to Indicator.*—The usual amount of indicator is added to a solution of 20 ml perchloric acid (55-per cent) in 200 ml water and titrated with ceric sulphate or potassium permanganate. It will be found to equal about 0.3 ml of 0.01154 *N* solution.

*Standardization of Arsenite.*—Ten ml of 0.03 *N* arsenite or 30 ml of 0.01 *N* solution are transferred to a beaker containing 25 ml perchloric acid (55-per cent) diluted to 200 ml. Six drops of osmic acid solution and 1 ml of phenanthroline ferrous perchlorate are added, and the solution is titrated with the standard (ceric sulphate) or potassium permanganate. The blank should be considered.

**Example:**

Arsenite used .....		10.0 ml
Permanganate used .....		30.3 ml
Blank .....		0.3
		<hr/>
		30.0
Factor of arsenite .....		3.00
For Low Chromium		
Arsenite used .....		30.0 ml
Permanganate used .....		30.3
Blank .....		0.3
		<hr/>
		30.0
Factor is 1.00		



## Calculation of Results:

High Chromium			
0.03 <i>N</i> Arsenite used	33.4	ml	
Permanganate equivalent ( $33.4 \times 3.0$ )	100.2	ml	
Permanganate used	6.2		
Blank	0.3	5.9	
Permanganate Chrome	94.3		
Chrome present			0.94 per cent
Low Chromium			
0.01 <i>N</i> Arsenite used	5.4	ml	
Blank	0.3	ml	
	5.1	ml	
Permanganate equivalent ( $5.1 \times 1.0$ )	5.1		
Permanganate used	3.5		
Blank	.3	3.2	
Permanganate Chrome	1.9		
Chrome present			0.019 per cent

If the accuracy desired is only 0.003 per cent, the 0.03 *N* arsenite may be used for low chrome.

The arsenite can also be standardized against purified  $K_2Cr_2O_7$ . For high chromium (12 per cent and higher), the arsenite is made 0.15 *N* and about 60 ml are required to reduce 18 per cent chromium on 1 g sample. Therefore, 0.5 g of the  $K_2Cr_2O_7$  is dissolved in 200 ml water, 6 drops of the osmic acid solution are added, followed by 60 ml of the arsenite solution, and the excess arsenite is titrated with standard  $KMnO_4$  solution.

# Determination of Vanadium

## Methods Available

Although the color method given at the end of this section may be applied with satisfactory results in the absence of titanium, in steel analysis the most reliable methods for vanadium are volumetric and depend upon either measured reduction of compounds of the elements from the quinquevalent to the quadrivalent stage, as in Johnson's and Kelley's methods, or in measured oxidation from the quadrivalent to the quinquevalent condition, as in the HCl reduction, or Compagne's method, and the ferrous sulphate-persulphate-permanganate method. In low-alloy steels some of these methods, particularly the last, are most conveniently applied after the determination of chromium and to the same solution. In high-alloy steels, however, two difficulties are encountered—one due to the fact that, while the vanadium is easily reduced, it is oxidized only with the strongest oxidizing agents and then but slowly in the cold; and the other due to color interference by salts of other elements, such as chromium, nickel, and even iron itself, which obscure the end point. With such steels, procedures involving at least partial separation of the vanadium from the interfering elements may be necessary to obtain accurate results; and particularly are such separations necessary if the percentage of vanadium is small. Up to 1935 no rapid and convenient method of separating the chromium from the vanadium in the original solution, leaving the latter in a condition suitable for titrating the vanadium, had been devised, so it is a pleasure to be able to include such methods in this book.

When a dilute acid solution of vanadium is treated with hydrogen peroxide, a reddish brown color is developed, and this reaction may be used in the determination of vanadium isolated from interfering substances. In steel solutions it is subject to interference by elements, the salts of which are highly colored and by other elements, such as titanium, that give characteristic colors with hydrogen peroxide. Color due to Ti can be bleached with HF or NaF, but not that due to Mo and Ce. The molybdenum color, however, does not interfere.

While these fundamental reactions appear simple, many variations have been introduced in their application, only a few of which have been selected for inclusion in the following procedures.

### Ferrous Sulphate-Persulphate-Permanganate Method

This method is applied immediately following the determination of the chromium, and the complete procedure has, therefore, been

given under the determination of the latter element. The method is not applicable without proper separations to steels containing tungsten, much chromium, or little vanadium on account of color interference. For low-chromium steels containing up to 5 per cent chromium, the procedure is briefly outlined as follows:

**Weight of Sample.**—2 g for chromium up to 2 per cent; 1 g for chromium from 2 to 5 per cent; 5 or 10 g for low vanadium (under 0.05 per cent) in carbon steels.

**Acid Mixture.**—Add 320 ml dilute  $\text{H}_2\text{SO}_4$  (1:1) and 80 ml  $\text{H}_3\text{PO}_4$  (85-per cent) to 600 ml water.

### Procedure

**Vanadium and Chromium-Vanadium Steels.**—Dissolve the sample in 50 to 60 ml of the acid mixture. Evaporate the solution and dissolve carbides by adding nitric acid, or by diluting, filtering, and fusing any residue with sodium carbonate, if necessary, and dissolving the melt in the solution. Dilute to 300 ml with hot water. Add 5 ml of a 1-per cent solution of silver nitrate and 10 ml of ammonium persulphate solution (30-per cent), then boil 8 to 10 minutes, adding more of these reagents and a few drops of a 2-per cent solution of  $\text{KMnO}_4$ , if no pink color develops. Add 5 ml of dilute  $\text{HCl}$  (1:1) or 10 ml of a 5-per cent solution of  $\text{NaCl}$  and boil for 5 minutes after the pink color fades and any  $\text{MnO}_2$  is dissolved. Cool, dilute to about 400 ml, and titrate chromium visually by adding an excess of ferrous sulphate solution and back-titrating with 0.05 or 0.10 *N* permanganate solution to an end point that does not fade for 1 minute. To overcome the errors due to dilution effect and the green color of the chromic salt formed, boil the solution 10 minutes, cool, and again titrate to the same end point. To find the number of ml of the  $\text{KMnO}_4$  solution equivalent to the chromium present, subtract this latter volume or blank from the first; then deduct the corrected volume from the ml of  $\text{KMnO}_4$  equivalent to the ferrous sulphate added. Calculate the per cent chromium, using the factor 0.01734 as the g of chromium equivalent to 1 ml of a normal solution.

To determine vanadium, which has been oxidized by the treatment given above, add 15 ml of 0.03 *N* ferrous sulphate solution. Test a drop with  $\text{K}_3\text{Fe}(\text{CN})_6$  solution, add more of the ferrous sulphate, if necessary, to give an excess, stir, and add 10 ml of a 15-per cent solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , which oxidizes the excess ferrous sulphate, but neither the chromium nor the vanadium. Titrate the cold solution with 0.02 *N* or 0.03 *N*  $\text{KMnO}_4$  solution to the same permanent end point as in the titration for chromium. Determine and subtract the blank as described above for chromium to find the permanganate required to titrate the vanadium present. Redetermination of the blank is necessary particularly because the permanganate solution is

more dilute than that used for chromium. To find the per cent vanadium, multiply 0.05095 (g of V equivalent to 1 ml of a normal solution) by the normality factor of the  $\text{KMnO}_4$  solution, by the number of ml of  $\text{KMnO}_4$  solution used, and by 100; and divide the product by the weight of sample used.

**Carbon Steels Containing Little Vanadium.**—Use 10 g of sample and make a bicarbonate separation as directed under *Chemical Separations*. Ignite and fuse the residue with sodium peroxide, dissolve in water, boil, filter on asbestos, wash with water containing  $\text{NaOH}$  and  $\text{Na}_2\text{SO}_4$ . Acidify with  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  and titrate as directed above for both chromium and vanadium.

**High-Chromium Steels.**—For low vanadium, use 10 g and dissolve in 250 ml of 8-per cent  $\text{H}_2\text{SO}_4$ ; for vanadium steels, use 2 g and dissolve in 150 ml. Cool to  $15^\circ\text{C}$ , add paper pulp, stir in a freshly prepared 6-per cent solution of cupferron till the precipitate takes on a reddish brown color. Filter, wash 12 times with 1-per cent sulphuric acid, transfer the paper to the original beaker, add 20 ml  $\text{HNO}_3$  and 10 ml  $\text{H}_2\text{SO}_4$ , and evaporate to fumes. Cool, add  $\text{HNO}_3$ , and evaporate as before. Cool, dilute to 300 ml, add 3 ml  $\text{H}_3\text{PO}_4$  (85-per cent), then add  $\text{KMnO}_4$  until the solution is pink. Complete the determination for vanadium as described above.

#### Perchloric Acid-Dibasic Potassium Phosphate Method

This method is a combination method for chromium and vanadium, applicable to steels containing up to 1.5 per cent chromium, and is given under *Methods for Chromium*. It consists in dissolving the sample and oxidizing chromium and vanadium with perchloric acid, reducing with ferrous sulphate, titrating the chromium with ortho-phenanthroline indicator, and subsequently removing the perchloric acid with potassium phosphate, and titrating the vanadium.

#### Method Eliminating Chromium as Chromyl Chloride

In this method all the chromium is volatilized and thus eliminated by properly introducing hydrochloric acid into a perchloric acid solution of the sample. After the chromium has been eliminated, the perchloric acid serves to oxidize the vanadium, which may be reduced and determined by adding an excess of ferrous ammonium sulphate of known reducing value and titrating the excess with a standardized solution of potassium permanganate. The treatments for the elimination of the chromium have been described under *Chemical Separations*. As the method provides no sharp end point to indicate when all the chromium has been volatilized and expelled from the containing vessel, care and practice are required to make sure that all the chromium has been eliminated before the direct titration of the vanadium can be attempted. However, by modifying the procedure for titrating the vanadium, the presence of chromium can be detected before the

vanadium is titrated. For these reasons the procedure is repeated in detail below.

**Special Solutions Required.**—*Standard Potassium Permanganate.* The salt is dissolved in water and treated to give a stable solution as described under *Chromium*. The concentration is varied according to the percentage of vanadium present and the precision desired. Usually when many determinations are to be made and also for routine work, it is desirable to regulate the concentration of the solutions so that 1 ml is equivalent to 0.1 per cent or 0.05 per cent vanadium on the basis of the weight of sample used. To put the  $\text{KMnO}_4$  solution on such a basis, the calculations involved are as follows:

$$\text{A normal solution of } \text{KMnO}_4, \text{Mn}^{+7} \rightarrow \text{Mn}^{+2} = \frac{158.026}{5} = 31.605 \text{ g per liter.}$$

1 ml of a normal solution = 0.05095 g of V,  $\text{V}_2\text{O}_5 \rightleftharpoons \text{V}_2\text{O}_4$ , or,

1 ml of a normal solution = 5.095 per cent V on 1-g sample.

Therefore, for 1 ml to equal 1 per cent V on 1-g sample, the normality must be  $\frac{1}{5.095} = 0.1963$ , and for 1 ml to equal 0.1 per cent V on 1-g sample, the normality is 0.01963. For a 2-g sample these values become 0.3925 and 0.03925, respectively. After the solution has been standardized against sodium oxalate by the approved method, the work of standardizing as well as the analytical technique is checked by analyzing an authoritative standard sample of steel.

*Ferrous Ammonium Sulphate Solution.*—This solution, prepared as described under *Chromium*, is of a concentration approximately 0.03 N, and the same solution may be used for V up to 1.5 per cent. Since the solution changes on standing, its permanganate value is determined each day it is used.

*Ammonium Persulphate Solution.*—Dissolve 15 g of the salt in 100 ml of water and use the solution fresh.

**Weight of Sample.**—For vanadium up to 1 per cent, use 2 g of sample, and 1 g for higher vanadium.

## Procedure

**Solution of Sample.**—Weigh and transfer the sample to a clean, dry, Erlenmeyer flask. For 2 g, add 10 ml of  $\text{HCl}$  and 50 ml of  $\text{HClO}_4$  (60-per cent). For 1 g, use 7 ml of  $\text{HCl}$  and 30 ml of the  $\text{HClO}_4$ . Cover the flask and heat to about  $100^\circ \text{C}$  until the sample has dissolved, then increase the temperature until the perchloric acid is condensing on the wall of the flask and maintain the solution at this temperature until the chromium is all oxidized. Volatilize the chromium by adding  $\text{HCl}$  or  $\text{NaCl}$  as described below, using  $\text{HCl}$ , preferably, to avoid high concentration of sodium perchlorate in the solution.

**Volatilization of Chromium by Additions of NaCl.**—When all the chromium has been oxidized, grasp the flask with tongs, remove the cover, and add about 1 g of sodium chloride, giving the flask a swirl as the salt is added. Continue the additions of the salt in the same manner until brown fumes of chromyl cease to be given off. Heat the flask until the  $\text{HClO}_4$  is again condensing on the wall, and repeat the addition of NaCl. When brown fumes no longer appear on adding the salt, cool the flask somewhat, and rinse the wall with a fine jet of water. Add 10 ml of the  $\text{HClO}_4$ , heat to fuming, and again add 2 or 3 portions of the NaCl, using for a 2-g sample about 10 g in all. Finally, cover the flask and heat until the condensing  $\text{HClO}_4$  has carried down any NaCl adhering to the wall of the flask and the resulting HCl has been expelled. Cool, dilute somewhat to hold salts in solution, and determine vanadium as directed below.

**Volatilization of Chromium by Additions of HCl.**—Grasp the hot flask with the tongs, remove the cover, give the flask a swirling motion, and, with the mouth of the flask directed away from the person, add 1 to 2 ml of concentrated hydrochloric acid at a time until brown fumes are no longer evolved. Then, cover and reheat the flask till  $\text{HClO}_4$  is condensing on the wall, and add HCl as before. Repeat these operations 3 or 4 times after visible brown fumes of chromyl chloride fail to appear on adding the HCl to the  $\text{HClO}_4$  solution. Finally, heat the flask until the  $\text{HClO}_4$  is condensing on the wall and the HCl has been expelled. Cool, add 20 ml of water to prevent crystallization, and proceed with the determination of V as directed below.

**Comparison of Titrating Solutions and Check for Chromium.**—Cool the solution to room temperature, transfer it to a 400-ml beaker, dilute to about 200 ml, and stir into it 5 ml of phosphoric acid. If it is certain all the chromium has been eliminated, omit the following titrations and proceed with the determination of vanadium as directed below. To reduce the vanadium and any chromium that may be present, add from a burette 10 ml of the ferrous ammonium sulphate solution, or proportionately more if vanadium is above 0.5 per cent, and titrate the excess with standard potassium permanganate solution until the solution assumes a faint pink color that does not fade for 1 minute of continuous stirring. If the 2 titrating solutions have not already been compared, add exactly the same volume of the ferrous ammonium sulphate, stir, and titrate as before to determine the permanganate solution equivalent to the ferrous sulphate. Compare the 2 titrations to detect the presence of chromium, adding 0.1 to 0.2 ml to the  $\text{KMnO}_4$  solution used in the first titration for end point blank.

**Titration of Vanadium.**—To reduce the vanadium, add to the solution the same volume of ferrous ammonium sulphate solution as was used in the last titration, and stir thoroughly. To oxidize the excess ferrous sulphate, add 8 ml of the ammonium persulphate solution and stir the contents of the beaker for 1 minute. Titrate the solution

slowly with the standard permanganate solution until a pink color develops that does not fade after 1 minute of vigorous stirring. Since the permanganate used is equivalent to the vanadium present, add to the volume of the former the ml required to obtain the same end point in a blank determination. Multiply the sum by the vanadium titer of the solution and by 100, and divide by the weight of sample used to find the per cent vanadium in the sample. If the permanganate is standardized to give the per cent vanadium direct, multiply the ml of permanganate by the percentage conversion factor.

### The Perchloric Acid-Lead Chromate-Potassium Phosphate Method <sup>1</sup>

#### Principle and Application

In this method the chromium is oxidized by digestion with perchloric acid and separated as lead chromate, following which operation the vanadium is reduced with ferrous sulphate, the perchloric acid is removed by adding potassium phosphate, and the vanadium is titrated with standard potassium permanganate in the presence of phenanthroline ferrous perchlorate. The method is applicable to stainless steels and others containing much chromium, and either high or low in vanadium.

Solutions required are given in a section following the procedure, which is as follows:

#### Procedure

**Solution of Sample and Separation of Chromium.**—Weigh 2 g of sample and transfer to a 400-ml beaker. Dissolve the steel in 20-25 ml hydrochloric acid (concentrated). Add 35 ml perchloric acid (55-per cent, free of sulphuric acid). Boil the solution until the fumes that form are expelled and the perchloric acid is condensing upon the wall of the beaker. Continue the heating at this temperature for 10 minutes longer to oxidize the chromium completely. Then, grasp the beaker with tongs and slide it upon a cold plate for 10 to 20 seconds. Then remove the cover, and while revolving the beaker, cool it by dipping it intermittently into running water. Add 70 ml of water, stir with a rod, boil 3 minutes, remove from the heater, and add 5 drops of silver perchlorate (0.5 M). Then add lead perchlorate (0.5 M)—

<sup>1</sup> The removal of chromium as lead chromate was suggested by Willard, H. H., and Gibson, R. C., *Ind. Eng. Chem., Anal. Ed.*, 3, 88 (1931). They, however, titrated the vanadium with ferrous sulphate and any chromate present caused an error. Willard, H. H., and Young, P., *Ind. Eng. Chem., Anal. Ed.*, 6, 48 (1934), suggested the direct titration of vanadium from  $V_2O_4$  to  $V_2O_5$  after reduction by ferrous sulphate and oxidation of excess ferrous sulphate by permanganate, and after buffering the solution with sodium acetate. C. V. Foerster of Duquesne Laboratory suggested removing the perchloric acid from solution by adding potassium phosphate.

6 ml for the first 100 mg and 5 mg for each additional 100 mg of chromium—and stir. Allow the mixture to stand hot for a half minute to coagulate the precipitate. Cool in running water, stirring occasionally. Filter into a 400-ml beaker. Wash with cold water and cool thoroughly.

**Removal of  $\text{HClO}_4$ , Reduction and Titration of Vanadium.**—To the solution, which is now almost free of chromium, add 7 ml phosphoric acid and 2 ml phenanthroline ferrous perchlorate. Then add ferrous sulphate to reduce any chromate present and to reduce the vanadium to  $\text{V}_2\text{O}_4$ . Add permanganate (about 0.01 *N*) rapidly until the red is bleached. The color may come back, but take the first decolorization, the object being to oxidize the excess  $\text{FeSO}_4$ , but not the  $\text{V}_2\text{O}_4$ . If this point is overrun, add a little  $\text{FeSO}_4$  until the color is red, and decolorize again with permanganate. If the amount of permanganate is less than 1 ml of 0.01 *N* solution, add a moderate excess of ferrous sulphate and reduce again as before, making sure that the permanganate this time is more than 1 ml. Take a reading. Add 20 ml of phosphoric acid and then add 35 ml of potassium phosphate solution while stirring.

The potassium precipitates as perchlorate, liberating the phosphoric acid to buffer the solution further. The solution turns red if vanadium is present.

Titrate with 0.01 *N* permanganate until the red color changes to a violet. The permanganate used in this last titration is a measure of the vanadium. One ml of 0.01 *N* solution equals 0.0005095 g or 0.025475 per cent on a 2-g sample and 1 ml of 0.01154 *N* solution equals 0.0294 per cent on a 2-g sample.

### Reagents and Solutions Required

**Perchloric acid, 55-per cent.**—Dilute the 68-per cent (sp. gr. 1.65-1.66) acid to 55 per cent (sp. gr. 1.47), requiring about 400 ml of water per liter, and decant or filter off any residue which may form if technical grade is used.

**Ferrous Sulphate-Phosphoric Acid Mixture.**—Dissolve 1 g of pure crystalline ferrous sulphate ( $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ ) in 1 liter of a 15-per cent solution of 85-per cent phosphoric acid, or add 6 g of the salt to 6800 ml of water and 1200 ml of 85-per cent phosphoric acid. The concentration need not be exact.

**Potassium Phosphate Solution.**—Dissolve 1 pound of dibasic potassium phosphate ( $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ) in 220 ml of water to make a 100-per cent solution. The solution serves to precipitate and remove the perchloric acid from solution and to replace it with phosphoric acid.

**Indicator Solutions.**—The indicator solution is prepared from ortho-phenanthroline ferrous sulphate which in turn is prepared from ortho-phenanthroline monohydrate, preferably by the procedure given on



pages 142 and 143, or by the methods recommended by G. Frederick Smith, which are as follows:

### Preparation of Orthophenanthroline Ferrous Sulphate as Given by G. Frederick Smith

**Materials.**—1. Orthophenanthroline monohydrate.  $C_{12}H_8N_2 \cdot H_2O$ , M. W. 198, M.P. 90-100° C. Use 14.85 grams for 1000 ml of 0.025 *M* solution as below.

2. Ferrous sulphate, 0.025 *M* solution. Use 6.95 grams of  $FeSO_4 \cdot 7H_2O$  in 1000 ml of solution. Make fresh as needed.

**Procedure.**—Dissolve the ferrous sulphate and add the orthophenanthroline monohydrate and stir until all is dissolved, giving a dark red solution.

One drop of this indicator serves for each titration in a volume of 100-150 ml. One thousand ml of indicator should serve for 15,000 to 20,000 titrations.

### Preparation of Orthophenanthroline Ferrous Perchlorate

Prepare the sulphate as directed above. Add dilute perchloric acid drop by drop until a bright red precipitate forms and the supernatant liquid is almost colorless. Filter, wash the precipitate 3 or 4 times with a little water, then wash it into a bottle, add a little very dilute perchloric acid, and use the saturated solution, always keeping an excess of the reagent present.

### Preparation of Lead and Silver Perchlorate, 0.5 M Solutions

Methods for the preparation of these solutions are given under *Chemical Separations*, but are repeated here for convenience.

Dissolve 1 pound of  $Pb(ClO_4)_2 \cdot 3H_2O$  in water and dilute to 970 ml, or prepare a solution as follows: Transfer 166 g of pure lead nitrate to a casserole and add 50 ml of water and 110 ml of perchloric acid (70- to 72-per cent, C.P. grade) or 25 ml of water and 135 ml of perchloric acid (55-per cent). Place the casserole on a sand bath and evaporate carefully to avoid overheating till fumes of perchloric acid appear, during which evaporation the lead nitrate will dissolve. Rinse the inner wall of the casserole with a fine jet of water and repeat the evaporation. Test the solution for nitric acid by adding a drop to a little of a solution of diphenylamine in concentrated sulphuric acid on a spot plate. If a blue color develops, rinse the wall of the casserole with 30 ml of water and repeat the evaporation and fuming until the test is negative. Cool, dilute to about 800 ml, filter, and dilute the filtrate to 1 liter.

Prepare the silver perchlorate in the same way, using 8.5 g of silver nitrate to make 100 ml of solution.

Note: Discoloration of the salts during the evaporation indicates an insufficiency of perchloric acid, and more should be added at once.

Lead perchlorate decomposes above  $100^{\circ}\text{C}$  and the heating should not, therefore, exceed that temperature. If the temperature is too high, there is formed an insoluble mass which cannot be dissolved. The treatment prescribed above produces a small amount of insoluble salts which may be discarded.

### Nitric Acid-Potentiometric Titration Method

In this method the vanadium, following solution of the steel in sulphuric acid, is oxidized with nitric acid and titrated direct by potentiometric methods, for which purpose either the Larrabee or the Kelly apparatus may be used. The method is applicable to vanadium, chrome-vanadium, and chrome-vanadium-tungsten steels, and is most convenient, but is said to give slightly low results, representing approximately 99.5 per cent of the vanadium present. For vanadium under 0.1 per cent, separations to concentrate the vanadium are necessary.

### Special Solutions Required

**Standard Potassium Dichromate Solution.**—Dissolve 0.9626 g of pure  $\text{K}_2\text{Cr}_2\text{O}_7$  (recrystallized and dried at  $150^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  or heated just to the fusion point) in water and dilute to 1000 ml. One ml = 0.1 per cent vanadium on a 1-g sample.

**Ferrous Ammonium Sulphate Solution.**—Add 8 g of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  to 900 ml of water and add 100 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1). The solution changes, and it is necessary to titrate a portion with the  $\text{K}_2\text{Cr}_2\text{O}_7$  solution each day an analysis is made.

### Procedure

Dissolve 1 g of sample in a 400-ml beaker with 100 ml of dilute sulphuric acid (1:4), and add nitric acid dropwise to oxidize the iron and tungsten. If the latter element is present, add an excess of 5 to 8 ml of the oxidant, and boil till the  $\text{WO}_3$  is a bright or light yellow in color. Without filtering, dilute to 200 ml with hot water, add 40 ml of  $\text{HNO}_3$ , and boil 35 to 40 minutes, letting the solution evaporate to between 100 and 125 ml. Cool, dilute to 300 ml with ice water to give a temperature for the solution of not more than  $10^{\circ}\text{C}$ , and titrate at once. Place the beaker beneath the burettes with the electrodes and stirrer immersed in the solution, turn on the motor and battery switches, and add ferrous sulphate solution till the galvanometer needle comes to zero. Then add a little excess, throwing the needle farther in the same direction, and back-titrate to zero with the dichromate solution. Subtract the ml of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution used from the ml of the same solution equivalent to the ferrous sulphate used to find the per cent vanadium in tenths.

## Electrolytic-SO<sub>2</sub>-Permanganate Method

### Principles and Application of the Method

In this method, which is accepted as an umpire or referee method, the vanadium, along with the chromium, titanium, phosphorus, copper, etc., is first precipitated and separated from most of the iron, manganese, etc., by dissolving in dilute sulphuric acid and precipitating with sodium bicarbonate. Following this separation, the precipitate is dissolved in dilute H<sub>2</sub>SO<sub>4</sub>, and the vanadium is separated from the chromium and any iron, nickel, cobalt, or molybdenum that may be present, by electrolyzing over a mercury cathode, then reduced with SO<sub>2</sub> and titrated with KMnO<sub>4</sub>. With low-alloy steels the method appears ideal, but with high-alloy steels the large proportion of chromium present gives trouble by rendering the mercury almost solid. The method for volatilizing the chromium promises a way out of this difficulty, if the initial treatment can be followed.

Standard potassium permanganate is the only special solution required, and it is the same as that used for the determination of chromium by the persulphate method.

### Procedure

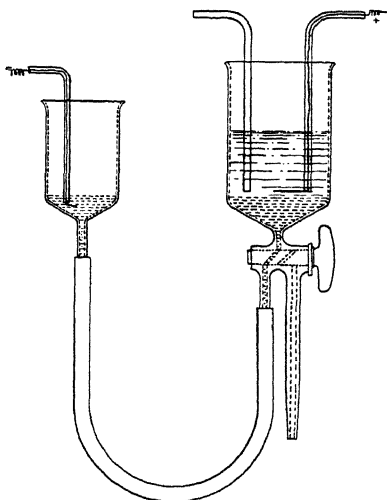
**Solution of Sample and Separation with Bicarbonate.**—Transfer 1 to 5 g of sample, depending upon the chromium and vanadium content, to a 300-ml flask and dissolve under cover with dilute sulphuric acid (100 ml diluted to 1 liter), using 20 ml for a 1-g sample and 10 ml additional for each additional gram of sample. As soon as action is complete, make a bicarbonate separation as described under *Chemical Separations*. After washing the precipitate 3 or 4 times with hot water, transfer both paper and precipitate to the Erlenmeyer flask, add 20 ml of nitric acid, shake to disintegrate the paper, add 5 ml of sulphuric acid, and heat to fumes. If the paper has not been completely destroyed, add 20 ml of nitric acid and repeat the operation to free the solution of all carbonaceous or organic matter. To eliminate any trace of nitric acid, cool, rinse the wall of the flask, and heat to fumes again. In the absence of tungsten, cool and dilute to 40 ml.

In the presence of tungsten, cool, dilute to about 30 ml, filter, wash thoroughly with 1-per cent sulphuric acid, treat the filtrate and washings as described below, and reserve the residue to test for vanadium, as described later.

**Electrolytic Separation of Vanadium.**—Neutralize with ammonia, adding a slight excess, bring back to neutral with H<sub>2</sub>SO<sub>4</sub>, and add an excess equivalent to 0.5 ml of the concentrated acid per 100 ml of solution. Transfer the solution to the electrolyzing apparatus with the cathode wire immersed in about 200 g of mercury, and electrolyze, using a current density of 0.16 amp. per cm<sup>2</sup> and stirring the solution almost constantly. Continue the electrolysis of the solution for 25

minutes, and test a drop of the solution for presence of iron with potassium ferricyanide solution. When the solution is free of iron, draw it off into a 150-ml Erlenmeyer flask, and without shutting off the current, wash the mercury 2 or 3 times with water. If necessary to remove particles of amalgam, pass  $\text{H}_2\text{S}$  and filter the solution. Boil to expel the  $\text{H}_2\text{S}$ . Add 2 to 3 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1), heat to  $75^\circ \text{C}$ , and add  $\text{KMnO}_4$  solution until a pink color persists.

FIGURE 13. Improved Melaven Electrolyzing Apparatus.



**Reduction and Titration of Vanadium.**—Heat the solution to boiling and pass a slow current of  $\text{SO}_2$  gas for 5 minutes. Continue to boil and pass a stream of oxygen-free  $\text{CO}_2$  gas until the escaping gas does not displace the color of 5 ml of water containing 1 drop of dilute sulphuric acid (1:1) and 1 drop of the standard potassium permanganate solution. Titrate at  $70^\circ \text{C}$  with standard  $\text{KMnO}_4$  solution and repeat the reduction with  $\text{SO}_2$  and the titration until results agree to 0.1 ml of the standard permanganate solution. Correct for a blank titration on a solution of the same volume and acidity. Then multiply the corrected volume by 100 times the vanadium titer of the  $\text{KMnO}_4$  solution and divide by the weight of sample used to find the per cent vanadium.

If tungsten is present, correct this result for any vanadium carried down with the tungstic acid, which is determined as follows: Dissolve the  $\text{WO}_3$  precipitate with  $\text{NaOH}$  solution, or ignite, volatilize  $\text{SiO}_2$  with  $\text{HF}$ , fuse with  $\text{Na}_2\text{CO}_3$ , and extract with water. Filter, if necessary, to clear the solution, and dilute to 80 ml. Add phosphoric acid (sp. gr. 1.37) until the solution is acid with 5 ml excess, and let it stand 2 hours.

In the meantime prepare a standard solution of vanadotungstic acid by dissolving 2.5 g of sodium tungstate in 100 ml water, adding sodium vanadate equivalent to 0.05 g of vanadium, diluting to 200 ml, adding 25 ml of  $\text{H}_3\text{PO}_4$  (sp. gr. 1.37), and diluting to 500 ml. Each ml thus equals 0.0001 g of vanadium.

Dilute the unknown solution to 100 ml. Add the standard solution from a burette to about 90 ml of water, and finally, adjust the color and volume to match the unknown. The ml of the standard used times 0.0001 gives the weight of vanadium, which is multiplied by 100 and divided by the weight of sample used to convert it to per cent. The vanadium held by the tungstic acid is equal to about 0.001 times the weight of W present.

### Color Method

This method is applicable only in the absence of titanium which gives a color with hydrogen peroxide, and other elements that give colored solutions under the conditions of the test. In the absence of the latter, approximate results for vanadium in the presence of titanium may be had by adding at the end a little NaF to bleach the color due to titanium.

### Special Solutions Required

#### Hydrogen Peroxide Solution

Sodium Peroxide .....	7 g
Sulphuric Acid (1:1) .....	250 ml
Water .....	750 ml

The water and acid are mixed and the sodium peroxide is added to the mixture in successive small portions. After each addition, the solution is cooled to room temperature.

#### Ammonium Vanadate Solution

Ammonium Vanadate .....	2.3 g
Water .....	1000 ml

The solution is standardized in the following manner: Fifty ml of the solution are diluted to about 300 ml with water and 10 ml of sulphuric acid are added. An excess of sulphurous acid or sodium sulphite is added and the solution is boiled until all the sulphur dioxide is expelled. The vanadium is determined by titrating the hot solution with standard potassium permanganate solution, and the volume of the solution is adjusted so that 1 ml = 0.001 g V.

### Procedure

**Solution of the Sample: Absence of Tungsten.**—Transfer 1 g of the sample to a 150-ml flask and add 40 ml of dilute  $\text{H}_2\text{SO}_4$  (1:4). Heat gently until the cuttings dissolve, then add 5 ml of dilute  $\text{HNO}_3$  (sp. gr. 1.20), and boil to the disappearance of brown fumes. To oxi-

dize organic matter and complete the oxidation of the vanadium, add 10 ml of a 5-per cent solution of ammonium persulphate and boil the solution until the excess of persulphate is decomposed (about 3 minutes). Cool to room temperature and add 5 ml of a 3-per cent solution of  $\text{H}_2\text{O}_2$ , which will develop a deep brown color if much vanadium is present. Transfer the solution to a comparison tube and dilute it until its color matches that of a standard solution prepared as described below. From the volume of the diluted solution, calculate the per cent vanadium in the sample.

*Preparation of Standards.*—Either a standard steel or a standard solution of ammonium vanadate may be used. The standard steel is of approximately the same composition as the sample of steel and is treated in the same way. After the solutions have been treated with  $\text{H}_2\text{O}_2$ , the solution of the standard steel is transferred to the comparison tube and diluted to a volume equal to some multiple of the per cent vanadium it contains. The per cent vanadium is found by dividing the volume of the sample by this multiple.

When the ammonium vanadate solution is used as a standard, 1 g of a plain-carbon steel standard, free of Ti, V, or other interfering elements, is dissolved like the sample. After the addition of the  $\text{H}_2\text{O}_2$ , chromium solution equivalent to the chromium in the sample is added, if the latter contains chromium, and standard ammonium vanadate solution is added from a burette until on mixing, the color matches that of the solution of the sample. The per cent vanadium in the sample is found from the number of ml of the standard ammonium vanadate solution used.

*Treatment of the Sample in the Presence of Tungsten.*—Treat the sample and separate tungsten as directed in the section on the *Determination of Tungsten*. To the filtrate from the tungstic acid, add 20 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) and evaporate to dense fumes. Cool slightly, add 5 ml of dilute  $\text{HNO}_3$  (sp. gr. 1.20), boil for 5 minutes, and complete the analysis as directed above for the solution of the sample oxidized with  $\text{HNO}_3$ .

# Determination of Molybdenum

## Methods Available

Molybdenum may be determined gravimetrically, volumetrically, or colorimetrically. In the absence of interfering elements, tungsten, or large percentages of copper or chromium, the last method does not require a preliminary separation of the molybdenum, but is applicable only to steels containing small proportions, under 1.00 per cent. Hence, only the first two methods are used in exact analyses of complex steels, and both involve either a separation of molybdenum as sulphide, or precipitation with alpha-benzoinoxime. The following procedure is applicable to the largest number of different types of steel.

## METHODS SEPARATING MOLYBDENUM AS SULPHIDE

### Weight of Sample

The weight of sample used is varied from 1 to 5 g, according to the probable percentage of molybdenum present, to give 20 to 30 mg of molybdenum.

### Procedure

**Solution of Sample.**—*Tungsten Absent.*—In the absence of tungsten, transfer the sample to a 600-ml beaker or flask and dissolve in 100 ml of dilute  $\text{H}_2\text{SO}_4$  (1:5) by heating gently until action ceases. Add 20 ml of a 25-per cent solution of ammonium persulphate and boil for 8 to 10 minutes to oxidize the molybdenum and part of the iron.

*Tungsten Present.*—In the presence of tungsten, dissolve the sample in 100 ml dilute  $\text{HCl}$  (1:1) and oxidize by adding  $\text{HNO}_3$ , dropwise, or by adding 20 ml of dilute  $\text{HNO}_3$  (1:1). Boil gently until the tungstic acid becomes a bright yellow, then either dilute to 150 ml or evaporate just to dryness, take up in 10 ml  $\text{HCl}$ , and add 50 ml of water. Heat to boiling, filter, and wash the residue with dilute  $\text{HCl}$  (1:9). Reserve the residue. At this point some prefer to add 15 ml  $\text{H}_2\text{SO}_4$  to the filtrate, evaporate to fumes, take up in 100 ml  $\text{H}_2\text{O}$ , and filter off any additional residue on a small filter, which is washed with 1-per cent  $\text{H}_2\text{SO}_4$ , this precipitate being combined with the previous one. If the original solution was evaporated just to dryness, this step may not be necessary.

To recover molybdenum from the residue of tungstic acid, fuse it with sodium carbonate and take up in water and filter, or dissolve the residue on the filter with hot 5-per cent solution of  $\text{NaOH}$ . In either

procedure, wash the paper with hot water, and once or twice with a little dilute  $\text{H}_2\text{SO}_4$ . Add 5 g tartaric acid to the filtrate or solution, then neutralize with  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , adding an excess of 3 ml of the former or 5 ml of the latter. Heat to boiling and pass  $\text{H}_2\text{S}$  for 10 minutes. Filter, wash with dilute acid (1-per cent) saturated with  $\text{H}_2\text{S}$ , and reserve to add to the main portion of the molybdenum sulphide obtained as directed below.

### Precipitation of Molybdenum as Sulphide

The solution containing the bulk of the molybdenum may be treated by either of the following procedures:

(a) Add 5 g tartaric acid, neutralize with ammonia, make just acid with  $\text{H}_2\text{SO}_4$ , and add 5 ml excess for each 100 ml of solution. Heat to boiling, pass  $\text{H}_2\text{S}$  for 30 minutes, dilute with an equal volume of hot water, continue to pass gas for 5 minutes, and digest at  $60^\circ \text{C}$  for 1 hour.

(b) To the oxidized solution, add ammonia until a slight precipitate of  $\text{Fe}(\text{OH})_3$  persists. Dissolve with a few drops of concentrated  $\text{HCl}$  and add 3 ml excess. Bring the solution to a boil and pass  $\text{H}_2\text{S}$  gas through it. If the  $\text{H}_2\text{S}$  produces a deep red color, add more  $\text{HCl}$ , not over 1 ml at a time, until the precipitate settles out readily. If the solution is too acid, the  $\text{H}_2\text{S}$  will not completely precipitate the molybdenum and the filtrate will be colored blue. In this event start the determination anew.

Separate the precipitate of sulphur and molybdenum sulphide by filtering through a close paper and wash with 1-per cent  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  saturated with  $\text{H}_2\text{S}$ .

If there is any doubt about the completeness of the precipitation of the molybdenum, boil to expel  $\text{H}_2\text{S}$ , and reduce the volume to about 300 ml. Add 20 ml of persulphate solution, boil for 10 minutes, and again pass  $\text{H}_2\text{S}$  for 15 minutes. Filter and wash as before.

### Treatment of the Sulphide

#### Absence of Arsenic, Vanadium, and Tin

**Ignition of  $\text{MoS}_3$  to  $\text{MoO}_3$ .**—Transfer precipitates to a silica or porcelain crucible and ignite slowly and carefully to constant weight at a temperature not over  $525^\circ \text{C}$ , as the oxide is volatilized at higher temperatures. Complete the determination by one of the following methods.

1. *Weighing Mo as  $\text{MoO}_3$ .*—To the crucible, add 10 ml 1:1  $\text{HCl}$  and digest until dissolved. Wash into a beaker and dilute to 50 ml with  $\text{H}_2\text{O}$ . Boil. Now add a 5-per cent solution of  $\text{NaOH}$ , until there are 2 drops in excess, using either litmus paper or phenolphthalein indicator. Filter, wash with hot water, burn off as before in the same crucible, and cool. Weigh. Subtract the weight of impurities from



the first weight, and calculate the difference to per cent Mo, using the factor,  $\text{Mo}:\text{MoO}_3 = 0.667$ .

2. *Precipitation and Weighing as  $\text{PbMoO}_4$* .—Leach in 30 ml of NaOH (4-per cent solution) for 30 minutes on a warm part of hot plate. Filter (suction, paper pulp) and wash free of NaOH, using phenolphthalein as indicator. Acidify with acetic acid, dilute to 100 ml, heat to the boiling point, and add sufficient lead acetate (4-per cent solution) to precipitate the molybdenum completely. Filter, preferably by suction, using paper pulp, and wash well with hot water. Burn off the paper slowly in the front of a muffle and weigh as lead molybdate.

$$\text{Per cent Mo} = \frac{\text{PbMoO}_4 \times 0.2614 \times 100}{\text{Weight of sample}}$$

### Presence of Arsenic, Vanadium, and Tin

Destroy the paper and oxidize the sulphide by digesting with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (5 ml) until the solution is clear and light colored. Evaporate and fume to expel all  $\text{HNO}_3$ . Cool and treat by one of the following methods:

1. *Gravimetric Method*.—Dilute to 100 ml, add 10 to 12 drops excess of a 20-per cent solution of NaOH, heat to boiling, and let stand 5 minutes. Filter, wash with hot water, heat the filtrate and washings to boiling, and pass  $\text{H}_2\text{S}$  for 10 minutes. Acidify with dilute  $\text{H}_2\text{SO}_4$  (1:1), add 4 ml per 100 ml excess, pass  $\text{H}_2\text{S}$  for 5 minutes, and digest at  $50^\circ \text{C}$  for 1 hour. Filter through a close paper, and wash thoroughly with 1-per cent sulphuric acid saturated with  $\text{H}_2\text{S}$ . Transfer the precipitate to a weighed porcelain crucible and ignite gradually to between  $500^\circ$  and  $525^\circ \text{C}$  until constant weight is obtained, but no higher, as  $\text{MoO}_3$  is volatile. Dissolve the  $\text{MoO}_3$  with dilute  $\text{NH}_4\text{OH}$  (1:1). If the solution is blue, indicating copper, estimate the amount as CuO by the color method and deduct from the weight of  $\text{MoO}_3$ . Wash the filter with water, ignite, and deduct the weight of any residue. Multiply the weight of purified  $\text{MoO}_3$  by 0.667 times 100 and divide by the weight of sample used to find the per cent molybdenum.

2. *Volumetric Method*.—Dilute to 50 ml, add 0.01 g  $\text{Fe}_2(\text{SO}_4)_3$ , then  $\text{NH}_4\text{OH}$  until the first appearance of a reddish tint dispelled by stirring, and heat the yellow solution to boiling. Heat 75 ml of dilute  $\text{NH}_4\text{OH}$  (1:1) nearly to boiling in a 250-ml beaker, and pour the solution into it, stirring constantly. Add paper pulp, filter, wash with hot water, and reserve the filtrate. Dissolve the precipitate with hot  $\text{H}_2\text{SO}_4$  (1:4), using as little acid as possible, then nearly neutralize, pour into  $\text{NH}_4\text{OH}$ , filter into reserved filtrate, and wash with hot water as before. Neutralize the combined filtrates with dilute  $\text{H}_2\text{SO}_4$  (1:1) and add an excess of 5 ml for each 100 ml of solution. Heat to boiling, add  $\text{KMnO}_4$  solution until decidedly pink, and pass through a Jones reductor, collecting the reduced solution beneath a solution of ferric

sulphate (0.1 to 0.2 g) and phosphoric acid (5 ml). Titrate with 0.03 *N*  $\text{KMnO}_4$  solution, subtract the blank, and calculate to per cent molybdenum. One ml 0.03 *N*  $\text{KMnO}_4$  solution equals 0.00096 g Mo.

**Separation and Determination of Molybdenum by the Alpha-benzoinoxime Method.**<sup>1</sup>—Alpha-benzoinoxime is almost a selective reagent for the separation of molybdenum under the proper conditions. After its precipitation, the molybdenum may be ignited to the oxide and determined gravimetrically or redissolved and estimated colorimetrically, the former method being applicable to molybdenum steels and the latter to carbon steels. The method was developed by H. B. Knowles of the National Bureau of Standards. The condensed procedure which was adopted in 1935 as a tentative standard by the American Society for Testing Materials is quoted below.

#### *Special Solutions Required*

*Alpha-benzoinoxime (2-per cent).*—Dissolve 10 g of alpha-benzoinoxime in 500 ml of ethyl alcohol. Filter if not clear.

*Boric acid (5-per cent).*—Dissolve 4 g of boric acid in 100 g of water.

#### *Procedure*

“Transfer a 1- to 3-g sample to a 600-ml beaker, add 50 ml of diluted  $\text{H}_2\text{SO}_4$  (1:6), and warm till action ceases. Carefully add just enough  $\text{HNO}_3$  (sp. gr. 1.42) to decompose carbides and to oxidize iron and molybdenum. Add 2 to 4 drops of HF, mix, and then add 10 ml of the boric acid solution. Boil for a few minutes and filter if the solution is not perfectly clear.

“Dilute to 100 ml with water, cool to 25° C, and add sufficient ferrous sulphate (0.5 g is usually sufficient) to reduce vanadic and chromic acids. Cool to 5° C, stir, and slowly add 10 ml of the alpha-benzoinoxime solution and 5 ml extra for each 0.01 g of molybdenum present. Continue to stir the solution, add just enough bromine water to tint the solution a pale yellow, and then add a few more ml of the benzoin reagent. Allow the beaker and contents to remain in the cooling mixture 10 minutes with occasional stirring, stir in a little macerated filter pulp, and filter through a rapid paper. If the first 50 ml or so are not entirely clear, this portion should again be filtered. Wash the precipitate with 200 ml of a cold, freshly prepared solution containing 25 to 50 ml of the prepared reagent and 10 ml of sulphuric acid in 1000 ml. On standing, needle-like crystals will appear in the filtrate if sufficient reagent has been employed.

“Transfer the precipitate and paper to a platinum crucible and cautiously dry. Char, without flaming, and ignite at 500 to 525° C. Cool, weigh, and repeat the heating until the weight remains constant. Treat the ignited residue with 5 ml of diluted  $\text{NH}_4\text{OH}$  (1 + 9), digest, and filter through a small paper. Wash well with diluted  $\text{NH}_4\text{OH}$

(1 + 99). Ignite the paper and contents in the original crucible, cool, and weigh. The difference in weights represents the  $\text{MoO}_3$  present.

"Tungsten is also precipitated. If present, the ammoniacal filtrate is treated as follows: Add 5 ml of diluted  $\text{H}_2\text{SO}_4$  (1 + 1) and evaporate to fumes of  $\text{H}_2\text{SO}_4$ . Cool, dilute to 25 ml with water, and add 1 to 2 ml of cinchonine solution [125 g of cinchonine dissolved in 1000 ml of diluted  $\text{HCl}$  (1 + 1)]. Digest at  $80^\circ$  to  $90^\circ$ , preferably overnight. Filter through a tight paper containing a little paper pulp and wash with cinchonine wash solution [30 ml of the cinchonine solution diluted to 1000 ml]. Transfer the paper and contents to a platinum crucible, char the paper, and ignite at  $750$  to  $850^\circ$  until constant weight is obtained. Cool, weigh, and subtract from the weight of  $\text{MoO}_3$  obtained previously.

"If Mo is present in very small amounts (plain-carbon steels), the ignited alpha-benzoinoxime precipitate should be dissolved in  $\text{NH}_4\text{OH}$  and the Mo determined colorimetrically.

"Note: If tungsten is present, it may be better to precipitate all of it with the molybdenum, ignite and weigh the two together, reprecipitate Mo with  $\text{H}_2\text{S}$ , as in the preceding method, and find the per cent tungsten by difference."

#### COLORIMETRIC METHODS

As previously stated, molybdenum up to 1 per cent is most conveniently determined by colorimetric methods for which there are several procedures. All are based on the red colored complex which quinquevalent molybdenum forms with sulphocyanate, and in modern practice all employ perchloric acid initially to effect solution of the sample. In routine work, direct comparisons by the naked eye are a trial on the eyesight and make the method subject to errors due to this cause. These objections are largely overcome by the use of colorimeters and all eyestrain is removed by the proper application of the electronic cell.

#### The "Photometer"

This instrument (patent applied for) by Sheard and Sanford is fully described by them in American Journal of Clinical Pathology, Vol. 3, No. 6, November, 1933, and is manufactured by Central Scientific Company, Chicago, Illinois. The different parts of the apparatus are shown in the following diagram. The intensity of the light must be constant, hence the current must be constant. A storage battery is most satisfactory. If line current is used, a constant voltage regulator is a necessary part of the equipment.

It depends upon the fact that when light of constant intensity is passed through a solution, the intensity of the transmitted beam is proportional to the concentration of the substance in solution. By use

of a special filter the instrument is made adaptable to the determination of both molybdenum and titanium, and may be adapted to others also. The instrument must be carefully calibrated for each substance, but once calibrated, the unknown sample is placed in the glass cell, inserted in the light path, and the reading on the milliammeter is translated into g per 100 ml or into per cent by reference to the calibration chart.

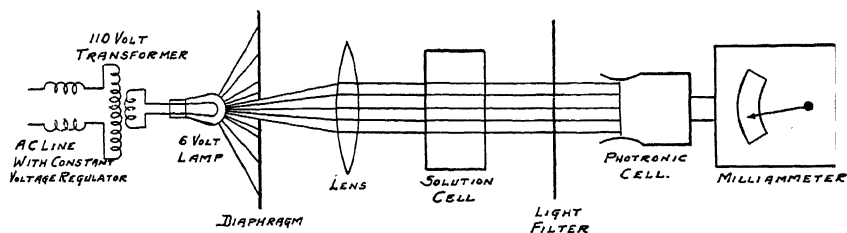


FIGURE 14. Diagrammatic sketch showing parts and illustrating principles of the "Photometer."

Several modifications of the method have been developed to meet various conditions, and to adapt the method to different steels. These procedures are given in detail as follows:

### A. Color Methods Extracting Molybdenum With Butyl Acetate

#### 1. Method Using the Photometer Special Solutions Required

##### Potassium Thiocyanate

Potassium thiocyanate, KCNS .....	50 g
Water .....	1000 ml

*Stannous Chloride.*—Add 250 g of  $\text{SnCl}_2$  to 200 ml of HCl (concentrated) and heat gently till the salt has dissolved. Cool somewhat and dilute the solution with 1200 ml of water.

*Saturated Butyl Acetate.*—This solution must be used fresh and is made up for each determination.

Add 50 ml butyl acetate to a separatory funnel containing 5 ml of the KCNS solution and 15 ml of the  $\text{SnCl}_2$  solution. Shake, allow to settle, and discard the aqueous solution.

**Procedure.**—Transfer 0.1 g of the sample to a 150-ml beaker, and cover with a raised watch glass. For carbon and low-alloy steels, add 5 ml of dilute  $\text{HNO}_3$  (sp. gr. 1.16) and 6 ml of  $\text{HClO}_4$  (70- to 72-per cent) and heat gently. For stainless steels, add, in addition to these acids, 10 ml of dilute HCl (1:1), and heat to boiling. When white fumes start to be given off, boil for 1 minute. Cool somewhat and

rinse the inner wall of the beaker with about 15 ml of water. Add 15 ml of the KCNS solution, agitate, and transfer the mixture to a 100 ml Squibbs separatory funnel, rinsing the beaker first with 10 ml of the  $\text{SnCl}_2$  solution and then with 20 ml of butyl acetate. Shake the funnel for 1 minute and discard the aqueous solution. Add 10 ml of the KCNS solution and 15 ml of the  $\text{SnCl}_2$ , and again shake for 1 minute. Draw off the wash solution. If the molybdenum present is under 0.50 per cent, transfer the butyl acetate solution to a 50-ml volumetric flask. If the molybdenum is between 0.50 and 1.00 per cent, make the transfer to a 100-ml flask. Dilute to the mark with saturated butyl acetate solution.

Thoroughly cleanse two Photometer absorption cells, add distilled water to one and a portion of the mixture containing the molybdenum to the other. Switch on the Photometer light several minutes before a reading is to be taken to fatigue the photoelectric unit. Place the cell containing the distilled water in the cell holder which supports it in the path of the beam of light, and adjust the intensity of the light with the diaphragm until the needle of the galvanometer reads 100. Replace the water cell with the one containing the colored butyl acetate solution, and record the reading of the galvanometer. To make sure the light intensity has not changed, again insert the water cell and note if the galvanometer still reads 100. If it does not, adjust it as before and take another reading for the colored butyl acetate solution. Convert the galvanometer reading to per cent molybdenum by reference to the calibration chart or table, which has previously been prepared for the Photometer.

## 2. Color Method Following Volatilization of Chromium and Separation of Molybdenum as Butyl Acetate

This method is designed to permit the determination of molybdenum in steels containing up to 30 per cent or more of chromium and up to 6 per cent molybdenum. Color interference from chromium is avoided by volatilizing this element at the beginning. In the development of the method (at Duquesne Works) the Lange Apparatus with a green screen was used. The use of such an apparatus avoids the constant use of standard samples as the per cent molybdenum can be determined from direct readings by reference to a conversion table or curve. To hold the molybdenum within the color range of the instrument employed, the weight of sample used is decreased as the per cent of molybdenum is increased. The accuracy depends upon a number of different factors, which become apparent from experience with the method.

**Special Solutions and Reagents Required.**—*Sodium Thiocyanate Solution (10 per cent).*—Dissolve 100 g of the salt in water and dilute to 1 liter.

*Stannous Chloride-Tartaric Acid Solution.*—Dissolve 350 g of  $\text{SnCl}_2$  crystals in a mixture of 200 ml  $\text{HCl}$  (concentrated) and 200 ml of water. Add 200 g of tartaric acid, agitate till the acid dissolves, and dilute to 1 liter.

**Procedure for Steels Containing up to 0.65 Per Cent Molybdenum.** For steels containing higher percentages, modify the following procedure as directed in the paragraphs at the end of this section.

*Solution of the Sample.*—Transfer 0.2 g of the sample to a 125-ml flask. Add 15 ml of  $\text{HClO}_4$  (55-per cent) and heat, gently at first. If the steel does not dissolve, add a little  $\text{HCl}$  or  $\text{HCl}$  and  $\text{HNO}_3$ . When the sample has dissolved, evaporate the solution rapidly to the fuming stage and continue the heating till chromium, if present, is all oxidized. In the absence of chromium, cool, and proceed as directed below under *Separation of Molybdenum*.

*Elimination of Chromium.*—In the presence of chromium, volatilize it by adding 1 g of  $\text{NaCl}$  in small portions to the fuming solution. If the sample contains more than 20 per cent chromium, rinse the wall of the flask with about 5 ml of the 55-per cent  $\text{HClO}_3$ , heat the solution to the fuming point, and again add 1 g of  $\text{NaCl}$  as before to expel most of the chromium remaining.

If it is desired to avoid a high concentration of sodium salts, substitute concentrated hydrochloric acid for the sodium chloride.

*Separation of Molybdenum.*—Cool the solution obtained as directed above and dissolve the salts by adding 25 ml of dilute sulphuric acid (1:6) and heating gently. When the salts have dissolved, again cool the solution, transfer it to a calibrated separatory funnel, and dilute to 35 ml with rinsings from the beaker. To separate the molybdenum and obtain it in solution for determination, proceed with the following operations in succession and without interruption: Add 5 ml of sodium thiocyanate solution, mix, add 10 ml of the stannous chloride-tartaric acid solution, and shake for 15 seconds. Add 100 ml (accurately measured) of butyl acetate and shake vigorously for 15 seconds. Finally, add 10 ml of sodium thiocyanate solution and 5 ml of the stannous chloride-tartaric acid solution, shake 30 seconds, and allow the liquids to separate. Draw off and discard the lower acid layer, which contains most of the iron and any of the chromium not volatilized in the initial treatments of the sample. To complete the separation, add 25 ml of dilute sulphuric acid (1:6), 5 ml of sodium thiocyanate solution, and 5 ml of stannous chloride-tartaric acid solution; then shake 30 seconds, and allow the liquids to separate. Draw off and discard the acid layer and permit a few ml of the colored solution to flow out also to cleanse the delivery tube of the separatory funnel. Using the remainder of the butyl acetate solution, proceed immediately with the colorimetric determination of molybdenum.

**Determination of Molybdenum with the Lange Colorimeter.**—To permit a few minutes' time for the instrument to adjust itself, turn

on the light just before making the first addition of sodium thiocyanate. With water in the cells on both sides of the colorimeter, balance the instrument by turning the nickel-plated knob until the needle points to zero. Close the shutter and turn the black knobs until the needle points to black 100 or red 2. Transfer the colored solution containing the molybdenum to a "cubette," or cell, and place it in the right hand side of the instrument. Take a reading, close the shutter, and adjust the needle to 100. Release the shutter and take another reading. To convert the reading to per cent molybdenum, refer to Table 2.

TABLE 2. CONVERTING READINGS OF LANGE COLORIMETER TO PER CENT

Per Cent	R	Per Cent	R	Per Cent	R	Per Cent	R
.01	2.0	.17	24 $\frac{3}{4}$	.33	38 $\frac{1}{2}$	.49	48 $\frac{1}{2}$
.02	4.0	.18	25 $\frac{1}{2}$	.34	39 $\frac{1}{4}$	.50	49.0
.03	6.0	.19	26 $\frac{1}{4}$	.35	40.0	.51	49 $\frac{1}{2}$
.04	8.0	.20	27.0	.36	40 $\frac{3}{4}$	.52	50.0
.05	9 $\frac{1}{2}$	.21	28.0	.37	41 $\frac{1}{4}$	.53	50 $\frac{1}{2}$
.06	11 $\frac{1}{2}$	.22	29.0	.38	42.0	.54	50 $\frac{3}{4}$
.07	13 $\frac{1}{2}$	.23	30.0	.39	42 $\frac{1}{2}$	.55	51.0
.08	14 $\frac{1}{2}$	.24	31.0	.40	43.0	.56	51 $\frac{1}{2}$
.09	16.0	.25	32.0	.41	43 $\frac{1}{2}$	.57	51 $\frac{3}{4}$
.10	17.0	.26	33.0	.42	44.0	.58	52 $\frac{1}{2}$
.11	18 $\frac{1}{2}$	.27	33 $\frac{1}{2}$	.43	44 $\frac{1}{2}$	.59	52 $\frac{3}{4}$
.12	19 $\frac{1}{2}$	.28	34 $\frac{1}{2}$	.44	45 $\frac{1}{2}$	.60	53.0
.13	20 $\frac{3}{4}$	.29	35.0	.45	46.0	.61	53 $\frac{1}{2}$
.14	22.0	.30	36.0	.46	46 $\frac{1}{2}$	.62	54.0
.15	23.0	.31	37.0	.47	47.0	.63	54 $\frac{1}{2}$
.16	24.0	.32	37 $\frac{1}{2}$	.48	47 $\frac{1}{4}$	.64	54 $\frac{3}{4}$
						.65	55.0

*For Steels Containing 0.65 to 1.00 Per Cent Molybdenum.*—Dissolve 0.1 g of the sample in 15 ml of 55-per cent  $\text{HClO}_4$  and treat once with  $\text{NaCl}$ . Multiply final results by 2.

*For Steels Containing 1.00 to 2.00 Per Cent Molybdenum.*—Dissolve 0.2 g of the sample in 20 ml of 55-per cent  $\text{HClO}_4$ . Volatilize the chromium. Dissolve salts in 25 ml dilute sulphuric acid (1:6), transfer the solution to a 100-ml volumetric flask, dilute to the mark, and draw out 25 ml into the separatory funnel. Add 5 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1), treat to separate, and determine the molybdenum as directed above; and multiply the final result by 4.

*For Steels Containing 2.00 to 6.00 Per Cent Molybdenum.*—Treat as directed above for steels containing 1.00 to 2.00 per cent molybdenum, but transfer to a 250-ml volumetric flask, dilute to the mark, and take 25 ml for the determination. Add 6 ml of dilute sulphuric acid (1:1), treat to separate and determine molybdenum, and multiply the final results by 10.

### 3. Method Estimating the Molybdenum Visually

**Special Solutions Required.**—*Sodium Thiocyanate (5-per cent).* Dissolve 50 g of the salt in 1000 ml of water.

*Stannous Chloride.*—Transfer 350 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  to a 500 ml Erlenmeyer flask, add 200 ml of diluted  $\text{HCl}$  (1 + 1), and boil gently until solution is practically complete. Transfer the solution to a liter bottle, dilute with freshly boiled  $\text{H}_2\text{O}$  to 1000 ml, add a few pieces of metallic tin, and stopper.

*Butyl Acetate.*—Saturate technical butyl acetate with  $\text{NaCNS}$  and  $\text{SnCl}_2$  by shaking and keep in a dark bottle.

*Standard Molybdenum Solution.*—Dissolve 0.5 g of pure  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in 1000 ml of water containing 5 ml of  $\text{H}_2\text{SO}_4$  and standardize by reducing 100 ml of the solution in a Jones reductor and titrating with  $\text{KMnO}_4$ . One ml of the solution should contain approximately 0.0002 g of Mo. The standard solution can also be made from National Bureau of Standards Sample No. 71 of calcium molybdate.

**Procedure.**—*Weight of Sample.*—For steels and irons containing 0.25 per cent or less of Mo, use 0.5 or 1 g of sample. For alloys containing 0.5 to 1.0 per cent, use a 0.5-g sample, and if over 1.0 per cent, a 0.2-g sample.

*Solution of Sample.*—Weigh and transfer the sample to a 150-ml Erlenmeyer flask. Add 20 ml of  $\text{HClO}_4$  (60-per cent) per 1 g of sample and warm until the sample has dissolved. Heat to boiling, cover, and fume until all carbonaceous matter has been destroyed. Cool somewhat, add 25 ml of water, and boil for a few minutes to expel free chlorine.

Add 2 g of tartaric acid and a slight excess of a 10-per cent solution of  $\text{NaOH}$ . Heat at about  $80^\circ$  for a few minutes. Remove from the source of heat, neutralize with diluted  $\text{H}_2\text{SO}_4$  (1 + 1), and then add an excess of 2 ml of the  $\text{H}_2\text{SO}_4$  (1 + 1) for each 9 ml of solution, which will give a solution of 10 per cent  $\text{H}_2\text{SO}_4$  by volume. Cool and transfer the solution to a 250-ml separatory funnel, rinsing out the flask with 10-per cent  $\text{H}_2\text{SO}_4$ . Add 10 ml of a 5-per cent solution of  $\text{NaCNS}$ . Mix quickly and add with 15 ml of the  $\text{SnCl}_2$  solution for a 0.5 g sample or 20 ml for a 0.1 g sample and shake well for 1 minute. Cool to room temperature, add 20 ml of treated butyl acetate, stopper, and shake well.

Alternately, the colored molybdenum complex can be extracted by adding 50 ml of ethyl ether, shaking, and drawing off the acid layer.

Allow the orange layer to separate and draw off the lower layer which can be discarded. On very low molybdenum material, add another portion of  $\text{NaCNS}$  and  $\text{SnCl}_2$ , mix in the separatory funnel, and again separate the orange layer. Transfer the orange layer into a Nessler tube, a Julian colorimeter tube (or other suitable comparison apparatus), and compare with a standard similarly carried through all steps of the procedure. If the orange layer is turbid, filter it through a layer of glass wool. The standard steel can be prepared by adding portions of a standard molybdenum solution to a molybdenum-free steel, or, a standard molybdenum steel can be used.



Note: For accurate comparisons, the concentration of molybdenum should not exceed 0.00005 g per ml of solution.

### B. Color Method Without Extracting Molybdenum

This method is designed for speed and safety, and is very rapid when the approximate composition of the steel is known in advance, as in heats made to chemical specifications.

#### Solutions Required

**Sulphuric-Hydrochloric Acid Mixture.**—Mix 100 ml HCl (1:1), 450 ml sulphuric acid (1:1), and 450 ml H<sub>2</sub>O.

**Perchloric Acid (55-per cent).**—Mix 600 ml of perchloric acid (68-70 per cent) with 250 ml of water, and test with a hydrometer. The sp. gr. should be 1.47.

**Sodium Thiocyanate (Sulphocyanate) Solution.**—Dissolve 50 g of pure sodium thiocyanate in water and dilute to 1 liter.

**Stannous Chloride Solution.**—Add 350 g of SnCl<sub>2</sub> · 2H<sub>2</sub>O to 200 ml of HCl (concentrated) and heat gently till solution is effected. Cool, dilute to 1000 ml with boiled water, transfer to a glass-stoppered bottle, and add a few small pieces of metallic tin.

**Chromium-Potassium Sulphate Solution.**—With the aid of heat, dissolve 4.8 g of crystallized chromium-potassium sulphate in 10 ml of dilute sulphuric acid (1:1), add 20 ml of water, boil till the solution assumes a green color, and dilute to 1000 ml.

**Ferric Sulphate-Hydrochloric-Sulphuric Acid Mixture.**—Add 70 g of anhydrous or 100 g of crystallized ferric sulphate to 150 ml of water, then add 120 ml of dilute hydrochloric acid (1:1), 400 ml of dilute sulphuric acid (1:1), and heat on a sand or water bath till the salt has dissolved. Cool the solution to room temperature and transfer it to a 1-liter volumetric flask.

**Ferromolybdenum Standard Stock Solution.**—This solution is prepared from a standard sample of ferromolybdenum, containing 57.20 per cent molybdenum. Other standards can be used by adjusting the weight accordingly.

Treat 1.05 g of this standard with 20 ml of dilute nitric acid (sp. gr. 1.20), and heat till dissolved. Add 20 ml of dilute sulphuric (1:1) acid, evaporate to fumes, cool, add 50 ml of water, and boil till solution is complete. Cool to room temperature, transfer to a 1-liter volumetric flask, add 100 ml of dilute sulphuric acid (1:1), and dilute to 1000 ml.

**Standard Solutions.**—From the 2 solutions prepared as directed above, make up 2 standard solutions as follows:

**Low Standard.**—25 ml = 0.15 per cent Molybdenum on 0.5-g Sample. To the ferric sulphate HCl · H<sub>2</sub>SO<sub>4</sub> acid mixture contained in the

1-liter flask, add 50 ml of the ferromolybdenum standard stock solution, and dilute to 1000 ml.

*High Standard.*—25 ml = 0.30 per cent Molybdenum on 0.5-g Sample. To the ferric sulphate  $\text{HCl} \cdot \text{H}_2\text{SO}_4$  acid mixture contained in the 1-liter flask, add 100 ml of the ferromolybdenum standard stock solution and dilute to 1 liter.

### Weight of Sample

To permit the highest accuracy with the two standards above, the weight of sample is varied as follows:

For 0.05 to 0.20 per cent molybdenum, use 0.5 g of sample and 25 ml of 0.15 per cent standard solution.

For 0.20 to 0.40 per cent molybdenum, use 0.5 g of sample and 25 ml of 0.30 per cent standard solution.

For 0.40 to 0.70 per cent molybdenum, use 0.25 g of sample and 25 ml of 0.30 per cent standard solution.

For molybdenum under 0.05 per cent, use 0.5 g of sample, 5 ml of the 0.15 per cent standard (= 0.03 per cent Mo), and extract the reddish molybdenum sulphocyanate with ether as directed in the method.

### Solution of the Sample

Transfer the sample to a 125-ml Erlenmeyer flask, add 10 ml of perchloric acid (55-per cent), cover, and heat gently till dissolved. When solution is complete, as ascertained by looking through the bottom of the flask, increase the temperature to boiling and fume 5 to 10 minutes, or until any chromium present is oxidized, as indicated by the change in color. Place the flask upon a cold plate for 10 seconds, and partly immerse in cold water for the same length of time. Add 25 ml of sulphuric-hydrochloric acid mixture and rotate the flask till the salts dissolve. Cool and transfer the solution to one of a pair of matched graduated comparison tubes, rinsing the flask with 5 ml of the acid mixture. Into the other tube, put 25 ml of either the 0.15 or the 0.30 standard molybdenum solution, add 8 ml of perchloric acid (55-per cent), mix, and mark the tube to indicate it is the standard.

### Estimation of Molybdenum: Absence of Tungsten and Copper

**A. Chromium Under 5 Per Cent or Absent.**—If chromium is present, add chromium-potassium sulphate solution to the tube containing the standard solution: 1 ml for each 0.1 per cent chromium present when a 0.5-g sample is used, and 0.5 ml for a 0.25-g sample. To both tubes, add 10 ml of the sodium thiocyanate solution from a burette, and mix by inverting the tubes 5 or 6 times. Then add 10 ml of stannous chloride to each tube and mix 8 or 10 times, but do not delay the operation for more than 15 seconds. Compare the colors, diluting the darker colored solution with cold dilute sulphuric acid

(1:6) until the colors match. Find the per cent molybdenum as in the example below.

**Example:**

Weight of sample 0.5 g	25 ml of 0.30 per cent (high) standard used
Volume of the standard	65.2 ml
Volume of unknown to match	68.6 ml

$$\text{Per cent molybdenum} = \frac{68.6 \times 0.30}{65.2} = 0.316$$

*Presence of Copper.*—If molybdenum is present, it is revealed at once by the dark red compound which quinquevalent Mo forms with thiocyanate (sulphocyanate). If copper is present, it forms a finely divided white precipitate, imparting a turbidity to the solution which can be detected by viewing it with yellow light. But the copper precipitate forms slowly, and if the comparison is made rapidly, it does not interfere if the molybdenum is above 0.10 per cent.

If copper interferes or the molybdenum content is very low, add pure ethyl ether to the tubes and shake. Continue to add ether and to shake until all the molybdenum complex as indicated by the color is extracted from the water solution. If the ether extends above the graduations on the tube, or if the color is very dark, close the mouth of the tube with the thumb, invert it, and when the ether rises, let some of the aqueous solution flow out by releasing the thumb pressure.

Continue the additions of ether until the colors match. Find the volume of ether in each tube by subtracting the reading at the top surface of the aqueous solution from the reading at the top of the ether.

$$\text{Per cent Mo in the sample} = \frac{\% \text{ Mo in the standard} \times \text{ml ether in the test}}{\text{ml ether in the standard}}$$

**B. Chromium and Chromium-Nickel Steels (Stainless and Heat-Resistant).**—For molybdenum under 0.5 per cent, the procedure given above is modified in one of three ways as follows:

*1. Special Solution Required*

*Chromium-Potassium Sulphate Solution.*—Add 48 g of chromium-potassium sulphate to 100 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) and heat gently until the salt has dissolved. Add 200 ml of water and boil the solution until it assumes a green color. Then, dilute to 1000 ml for use.

Substitute this solution for the more dilute solution used in A above and add 1 ml for each 1 per cent chromium present.

*2. Separate the chromium as lead chromate by modifying the method as follows:* Transfer 0.5 g of the sample to a 200-ml beaker, then dissolve the steel and oxidize the chromium by fuming with  $\text{HClO}_4$ , and precipitate the chromium with lead perchlorate as described for manganese and titanium when chromium is to be sepa-

rated by this method. Wash the lead chromate, using as little water as possible, and heat the filtrate to boiling. Add 2.5 ml of dilute hydrochloric acid (1:1) and 10 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) to precipitate as sulphate most of the lead remaining in solution. Heat almost to boiling for 4 or 5 minutes. Cool and filter the solution and wash the filter 3 or 4 times with a minimum amount of water. Transfer the filtrate to one of a pair of comparison tubes and add standard solution and 8 ml of perchloric acid to the other, omitting, of course, the chromium solution. Cool the solutions, then add 10 ml of the sodium thiocyanate and 10 ml of the stannous chloride solution, and compare as directed in the method for steels containing less than 5 per cent chromium.

3. Separate the chromium by volatilizing it as directed under *Chemical Separations*, using concentrated HCl instead of NaCl, and complete the determination as in the absence of chromium.

**C. Presence of Tungsten: Tungsten Steel.**—The following procedure is applicable to tungsten steels containing little molybdenum (under 0.7 per cent), but not to the tungsten-molybdenum steels. Transfer 0.5 g of the sample to one of two 125-ml Erlenmeyer flasks, and the same weight of a standard steel (see below) to the other. Add 10 ml of "phosphodant" (1 volume perchloric acid, 70-per cent, and 2 volumes of orthophosphoric acid, 85-per cent), and heat till the steel is dissolved. Add 5 ml of 70-per cent perchloric acid, and continue heating at fuming temperature for 10 minutes with the perchloric acid condensing on the wall of the flask. Cool, take up with 25 ml of sulphuric-hydrochloric acid mixture as directed above, and compare as follows:

After transferring the solutions to the comparison tubes, add to the standard, which contains approximately the same percentage of tungsten and chromium as the sample to be analyzed, but much less molybdenum, a volume of the standard molybdenum solution approximately equal to the molybdenum in the sample of steel. For example, if the sample contains between 0.20 and 0.30 per cent molybdenum, and the standard contains 0.02 per cent, add 2 ml of the standard solution, which is equivalent to 0.24 per cent molybdenum, to the standard steel and consider it as containing 0.26 per cent molybdenum. Compare and calculate the per cent molybdenum as directed for the method in the absence of tungsten.

In the case of unknown steels, add the stannous chloride, then add standard molybdenum solution until the colors are approximately the same. Note the volume of standard solution used, then adjust the volumes accurately and find the per cent molybdenum in the usual way.

#### Text Reference

1. National Bureau of Standards, *Journal of Research*, 9, (1932). Research Paper No. 453. Proposed as American Society for Testing Materials Tentative Standard Method. March, 1935.

# Determination of Titanium

## Methods Available

Titanium may be determined gravimetrically, volumetrically, or colorimetrically.

**In the gravimetric methods** it is always weighed as  $\text{TiO}_2$ . In pure solutions of its salts it is obtained by precipitating with ammonia. In solutions containing no copper, columbium, ferric iron, tantalum, thorium, tin, quadrivalent uranium, vanadium, or zirconium, it may be separated with cupferron (ammonium nitrosophenylhydroxylamine,  $\text{C}_6\text{H}_5\text{N}-\text{NO} \cdot \text{ONH}_4$ ) and ignited to  $\text{TiO}_2$ , provided the interfering elements bismuth, cerium, ferrous iron, lead, mercury, silver, thorium, and tungsten are absent, and silica, phosphoric acid, alkaline earths, or alkali salts are not highly concentrated in the solution. It is also obtained by hydrolysis with different reagents as follows:

- (1) On boiling its solutions saturated with sulphurous acid, the precipitation being incomplete in the presence of zirconium, or,
- (2) From such reduced slightly acid solutions treated with phenylhydrazine, which also precipitates aluminum, chromium, thorium, and zirconium, and all or a part of the phosphorus and vanadium and varying amounts of beryllium, cobalt, nickel, and tungsten, depending upon the concentration of the latter group.

**In the volumetric method** quadrivalent titanium is obtained in sulphuric acid solution as the sulphate,  $\text{Ti}(\text{SO}_4)_2$ , and reduced with zinc in a Jones reductor to trivalent titanium sulphate,  $\text{Ti}_2(\text{SO}_4)_3$ , which is oxidized with ferric sulphate. The solution must be free of other reducible elements, namely trivalent or hexavalent chromium, columbium, ferric iron, molybdenum, platinum, tungsten, vanadium, or uranium, and interfering elements such as nitric acid, organic compounds, polythionates, antimony, arsenic, and tin. A little platinum may do no harm, as it is reduced to the metallic state and remains in the reductor. The quadrivalent titanium sulphate may also be reduced with hydrogen peroxide and titrated with ferric sulphate, with the aid of suitable indicators, but this method is considered inaccurate and suitable only for control work, though it is subject to fewer interferences than the zinc reduction method.

**In colorimetric methods** the quadrivalent titanium in solution with sulphuric or perchloric acids, or mixtures of these with phosphoric acid solution, is reduced with hydrogen peroxide, and the titanium is estimated by comparing the color with that of a standard solution prepared with the same acid as the unknown, or the same proportions of

any two or all three of these acids. The color is masked by cerium and vanadium, which also develop characteristic colors with  $\text{H}_2\text{O}_2$ , and by molybdenum, chromium, copper, iron, and nickel, the salts of which may give colored solutions. The color due to ferric iron is overcome with phosphoric acid, which also affects slightly the color of the elements reduced with  $\text{H}_2\text{O}_2$ . In perchloric acid solution, nickel does not appear to interfere, but chromium must be separated. The color is affected by temperature, and that of titanium is rapidly bleached by hydrofluoric acid or by sodium fluoride, which form double fluorides ( $\text{M}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$ ) with reduced titanium. Satisfactory comparisons are limited to 0.01 g Ti per 100 ml of solution (1 per cent on 1-g sample), the color at higher concentrations being too dense for this purpose. Since most of these drawbacks can be overcome and as the method is quicker than either the gravimetric or the volumetric methods, it is the one generally used, except for standardization or referee work, and will be given first.

#### COLORIMETRIC METHODS

From the remarks above, it is evident that care must be taken to avoid misapplication of the color method for titanium. Hence, during the years it has been in use many modifications have been made to adapt it to different steels, ranging from plain-carbon steel to the complex alloy steels. In analyzing the latter, interfering elements must be separated before the method is applied.

#### Apparatus

Satisfactory results can be had by naked eye comparisons, for which no special apparatus is required except a set of suitable comparison tubes, which should have a total volume capacity of at least 50 ml, and be calibrated in 0.1 ml from 20 ml to 50 ml. When determinations must be made regularly, however, eyestrain is relieved and accuracy increased by the use of a suitable type of colorimeter, or the Photometer recommended for the determination of molybdenum. Among the many instruments, the Sargent and the Lange Colorimeters have been found satisfactory.

#### Special Solutions Required

**Standard Titanium Solutions.**—In the following methods either standard titanium sulphate or standard titanium perchlorate solutions are used, according to the requirements of the method employed in analyzing the steel. Since these solutions must be prepared in advance, methods for their preparation are given first. In all cases these solutions are adjusted to contain 0.5 g of Ti per liter = 0.0005 g per ml, so that 1 ml = 0.10 per cent Ti on 0.5 g sample.

**Standard Titanium Sulphate Solution.**—This solution may be prepared either from ignited titanous acid,  $\text{TiO}_2$ , or from recrystallized

potassium titanium fluoride,  $K_2TiF_6 \cdot H_2O$ . If the former is used, fuse 1 g with 15 g of sodium carbonate, leach the melt with hot water, filter on a 9-cm close paper, and wash the insoluble sodium titanate 2 or 3 times with hot water. Using a fine jet of water, wash the titanate back into the beaker and dissolve by heating with 200 ml of dilute sulphuric acid (1:1).

If the fluoride is used, transfer 2.7 g ( $2.7 \text{ g} = 0.5 \text{ g Ti}$ ) to a platinum dish, add 100 ml of  $H_2SO_4$ , heat gradually to the fuming stage, cool, rinse the inner wall with water, added carefully to avoid spattering and injury to the person, and again evaporate to strong fumes. Repeat these operations 3 times to drive off all fluorine, then cool, and add with constant stirring to 700 to 800 ml of water.

Transfer the titanium solution to a 1-liter volumetric flask, cool to standard room temperature of  $20^\circ \text{C}$  to  $25^\circ \text{C}$ , and dilute to the mark. To standardize the solution withdraw 2 or more 50-ml portions with a pipette graduated against the flask, dilute to 250 ml, heat to boiling, add a slight excess of ammonia, boil 2 or 3 minutes, filter on a close paper, wash 3 or 4 times with water, ignite gradually to  $1200^\circ \text{C}$ , cool, and weigh as  $TiO_2$ , 59.95 per cent of which gives the Ti present. Divide the weight of Ti by 50, multiply by the ml of solution left, and divide by 0.0005 to find the volume to which the remaining solution must be diluted. Add the required amount of water, and repeat the test to check the concentration.

**Standard Titanium Perchlorate Solution.**—This solution is somewhat difficult to prepare because the solubility of titanium perchlorate is limited and the concentration of the saturated solution is low, so that in dissolving sodium titanate with perchloric acid some of the titania is likely to precipitate. To prepare a standard solution, 1 ml of which is equivalent to 0.0005 g of titanium or 0.000834 g of  $TiO_2$ , the following procedure is suggested:

Transfer 1.1 g of titania,  $TiO_2$ , to a 30-ml platinum crucible containing 20 g of  $Na_2CO_3$ . Mix well and fuse over a blast lamp until the melt is perfectly clear. Tilt the crucible, insert a platinum rod, and let the melt solidify. Heat the crucible to detach the cake, and transfer it to a 400-ml beaker containing 250 ml of hot water. Apply a gentle heat to the beaker until the cake has disintegrated. Also, fill the crucible with hot water, heat, and add this and the crucible washings to the beaker. Filter and discard the filtrate, washing the sodium titanate 2 or 3 times with water. Then, transfer the residue to a 1-liter beaker, and add 600 ml of hot  $H_2O$  and 200 ml of perchloric acid (70-per cent, free of sulphuric acid). Also, wash the crucible with perchloric acid diluted with 3 parts of water. To dissolve the sodium titanate, digest on a sand bath for 1 to 2 hours or until the solution is almost clear. Add some paper pulp and filter the solution into a 1-liter flask. Wash neither the filter nor the beaker. Since this procedure

brings into solution more than 0.9 g of the titania, cool the solution in the flask to 20° C, and dilute this solution to 1000 ml with water at the standard temperature of 20° C.

To standardize the solution, proceed with duplicate determinations as follows, since  $\text{TiO}_2$  precipitated with  $\text{NH}_4\text{OH}$  will also contain a trace of iron, which is generally present. Withdraw 50 ml with a pipette and transfer it to an 800-ml beaker. Dilute to 400 ml and add 15 ml of hydrogen peroxide (3-per cent). To the colored solution, add  $\text{NH}_4\text{OH}$  until the color changes, then 1.5 ml of  $\text{HCl}$ , 30 ml of sodium thiosulphate solution (18-per cent), and 10 ml of acetic acid. Boil the solution for 10 minutes, filter, and wash the filter and precipitate with a 2-per cent solution of acetic acid. Ignite, gently at first, until the paper is burned, then at about 1000° C for 1 hour. Cool and weigh as pure  $\text{TiO}_2$ , and multiply by 0.5995 to find the weight of Ti in a 50-ml portion of the solution. To find the weight of the Ti in the solution remaining (900 ml, if the test has been made in duplicate), multiply this product by 20 (giving the weight in the original volume), and by the total volume remaining divided by 1000; that is, if 100 ml were used, make the calculation thus:

$$20 \times \frac{900}{1000} = 20 \times 0.9 = 18.$$

To find the volume to which the solution remaining must be diluted, divide the weight of titanium it contains by 0.0005 and from this volume subtract the volume remaining to find the volume of water to add so that 1 ml of the solution will contain 0.0005 g of Ti.

#### **Rapid Determination of Titanium and Titania by Color in Carbon Steels; Vanadium Absent**

The following procedures, designed for maximum speed, are applicable to carbon steels and others containing titanium and no interfering elements, except known low percentages of vanadium. They are not applicable to alloys containing much titanium, because perchloric acid is used to dissolve the sample and the solubility of the element in this acid is limited. The procedure is varied according to the percentage of titanium present as follows:

##### **Special Solutions Required**

For steels containing vanadium, prepare a standard solution of ammonium vanadate and add, after solution of the steel has been effected, a quantity equivalent to the vanadium in the sample used.

**Perchloric Acid (55-Per Cent).**—Preferably prepared by diluting the 70-per cent grade to a specific gravity of 1.47, requiring about 400 ml of  $\text{H}_2\text{O}$  per liter of acid.



### Procedure for Titanium Over 0.02 Per Cent

Transfer 0.5 g to a 150-ml flask, add 12 ml of perchloric acid (55-per cent), heat gently till solution is effected, and boil down to fumes to destroy organic matter. Cool, add 15 ml of water, and boil 2 minutes. Cool in running water, and transfer the solution to one of a pair of comparison tubes, rinsing with a little water to a volume of about 30 ml. Add 6 to 7 ml of perchloric acid to the other tube and dilute to the same volume.

Add 5 ml of a 3-per cent solution of hydrogen peroxide to each tube and mix the solutions thoroughly. Note the color that develops in the solution of the sample, which will be distinguishable if titanium exceeds 0.02 per cent. From a burette add carefully estimated portions of standard titanium perchlorate solution, mixing after each addition, until the colors match. Record the total number of ml of the standard solution used and multiply by 0.1 to find the per cent titanium in the sample. To test for vanadium, add NaF, which will cause the color from titanium to fade. If the color does not fade out completely, it is partly due to V and the result is not reliable.

### Procedure for Titanium Under 0.02 Per Cent

For titanium under 0.02 per cent it is necessary to use a large sample and separate the titanium from most of the iron. This separation may be effected by means of cupferron as described under *Separations*, or by the following method, permitting the determination of the titanium present as Ti or as titanium compounds soluble in HCl and as  $\text{TiO}_2$ .

### Solution of Sample and Separation of $\text{TiO}_2$

Dissolve 5 g of the sample in 100 ml of dilute hydrochloric acid (1:3) contained in a 400-ml beaker, heating gently as necessary to hasten solution. Filter on a close paper, and wash the paper 3 or 4 times with hot water. Reserve the filtrate and washings, and ignite the filter in a platinum crucible. Fuse the residue with a little sodium carbonate and leach or dissolve the melt in water. Acidify the leachings with sulphuric or perchloric acid, and determine titanium present as  $\text{TiO}_2$  separately as directed for titanium over 0.02 per cent, or acidify with hydrochloric acid and add to the filtrate and washings for total titanium.

### Separation of Titanium

To the filtrate or to the combined solutions, add 20 ml of a 10-per cent solution of ammonium phosphate and ammonia until a slight precipitate appears. Add 1.5 ml of hydrochloric acid and stir, when the precipitate should dissolve slowly. Add 30 ml of a 50-per cent solution of sodium thiosulphate solution, follow with 10 ml of acetic acid, and boil 10 minutes, which treatment will precipitate the titanium, aluminum and all or part of the vanadium and chromium, if all are present,

and some of the iron. Let the precipitate settle, then filter the solution and wash the filter 3 times with water, discarding the filtrate and washings.

Transfer the wet paper and contents to a 100-ml beaker, cautiously add 10 ml of perchloric acid (70-per cent), heat gently till the paper chars, then increase the temperature to the fuming point, and hold at this temperature till the solution is clear. Cool, add 15 ml of water, transfer to one of a pair of matched comparison tubes, rinse the flask with water, and dilute to about 30 ml. Complete the determination as described for titanium over 0.02 per cent and divide the final result by 10 to find the per cent titanium in the sample.

### Perchloric Acid-Lead Chromate-Hydrogen Peroxide Method for Chromium Steels: Color Method

#### Visual Comparison

In the absence of vanadium or much copper, this method is applicable to all steels, particularly of the stainless and heat-resistant types.

**Special Solutions Required.**—*Lead Perchlorate Solution.*—This solution (0.5 *M*) is prepared as described under the corresponding method for vanadium (see page 162) and under *Chemical Separations* (see page 63).

*Blank Solutions.*—To provide a blank solution for making the comparisons, a titanium-free steel, otherwise of about the same composition as the steel to be analyzed, should be carried through all steps in parallel with the sample. In place of this a specially prepared solution may be used. For the nickel solution, dissolve 5 g of nickel in perchloric acid and dilute to 1000 ml. On the basis of a 0.5 g sample, 1 ml of this solution equals 1 per cent nickel.

**Procedure.**—Transfer 0.5 g of the sample to an Erlenmeyer flask, add 12 ml of perchloric acid (60-per cent, vacuum distilled, free of  $\text{H}_2\text{SO}_4$ ), and heat gently till dissolved. When the sample has dissolved, increase the temperature to boiling and boil till the solution begins to fume. If the color changes, indicating chromium, cover the flask and continue the boiling for 10 minutes. Remove the flask from the heat, swirl, and immerse it in water to cool the contents quickly. Add 25 ml of water, boil 3 minutes, remove from the heat, and add a few drops of silver perchlorate. Then, add enough 0.5 *M* lead perchlorate solution to precipitate the chromium, rotating the flask to stir the contents during this addition.

The amount of the lead perchlorate solution required is 4 ml for each 100 mg of chromium present, plus 1 ml. To provide a safe excess for 0.5 g sample, 6 ml are added to the high-chromium heat-resistant steels, 5 ml to the 18-8 type, 4 ml for ordinary stainless steels, and 3 ml to the low-chromium steels.

Cool the solution rapidly and filter through a 9-cm loose paper into a 100-ml beaker. Wash the flask and the filter with a little water (5 ml) and transfer the solution to one of a pair of matched comparison tubes. Add to the other tube, 5 ml of perchloric acid of the same grade as that used to dissolve the steel, 5 ml of the lead perchlorate solution, and 1 ml of the nickel solution for each 1 per cent of nickel present. Dilute this mixture to same volume as the sample to be analyzed and cool both solutions to the same temperature, not over 25° C. Add 5 ml of 3-per cent hydrogen peroxide to each, mix thoroughly, and then add the standard solution of titanium perchlorate to the blank and the same volume of dilute perchloric acid (16 ml of 70-per cent diluted to 100 ml) to the sample until the colors match with the volumes equal, mixing thoroughly after each addition. To find the per cent titanium, multiply the ml of standard solution added to the blank by 0.10.

The result will be affected by vanadium. To test for this element, add 2 ml hydrofluoric acid or, preferably, 5 ml of a 10-per cent solution of NaF and observe the color change. If the color does not fade completely, or leaves a reddish color indicating vanadium, repeat the analysis using another method, preferably the second method following, which employs cupferron for the preliminary separation.

### Comparison by Lange Colorimeter

**Solutions Required.**—Refer to preceding method.

**Weight of Sample.**—The following method is designed for a 2-g sample containing from 0.01 to 0.65 per cent titanium.

For steels containing between 0.65 and 1.25 per cent titanium, use a 1-g sample, dissolve in 20 ml of  $\text{HClO}_4$  (55-per cent) instead of 35 ml, continue as directed below and multiply the result by 2.

**Procedure.**—Transfer 2 portions of the sample, each weighing 2 g, to separate 350-ml Erlenmeyer flasks and treat both as follows: Add 35 ml of dilute  $\text{HClO}_4$  (55-per cent) and heat to dissolve the cuttings, add a little  $\text{HCl}$  or  $\text{HNO}_3$  as may be necessary to hasten solution. When the cuttings have dissolved and the color of the solution has begun to change, cover the flask, heat till the acid is fuming strongly, and continue for 10 minutes with the acid condensing and flowing down the wall of the flask.

Cool the solution as rapidly as possible, add 40 ml of water, and boil 3 minutes. Remove the flask from the heat and add at once sufficient lead perchlorate solution (see preceding method) to precipitate the chromium completely. Shake and cool thoroughly, continuing to shake while cooling. Filter the solution into a 100-ml volumetric flask, and wash the flask and filter with a little water.

For a blank, dilute one of the samples to the mark with water, adding in advance of dilution a little sodium arsenite solution, if it shows a color indicative of chromium due to incomplete separation. Transfer the solution to a thoroughly cleaned cubette.

To the second sample add 5 ml of a 3-per cent solution of hydrogen peroxide, shake, dilute to the mark, and transfer to a thoroughly cleaned cubette for comparison.

With water in the cells on both sides of the instrument, balance the colorimeter by adjusting the nickel knob until the needle is over the zero mark.

Remove the cubettes containing the water blanks and place the cubette containing the solution of the steel to which hydrogen peroxide was added in the right-hand side, and the cubette containing the steel blank solution in the left-hand side. Using a green light filter, close the shutter and adjust the black knobs until the needle points to Black 100 or Red 2. Release the shutter and take the reading. To find the per cent titanium in the sample, refer to Table 3.

Note: This table is based on a residual vanadium content of 0.03 per cent, most common in steels highly alloyed with chromium. If the sample contains no vanadium, the result for titanium will be low; if it contains more vanadium, the result will be correspondingly high. The blank sample may be used for the determination of vanadium by adding ferrous sulphate and proceeding as directed under vanadium in stainless steel.

TABLE 3. PER CENT TITANIUM IN SAMPLE CORRESPONDING TO READINGS ON THE LANGE COLORIMETER. BASED ON 2-G. SAMPLE CONTAINING 0.03 PER CENT VANADIUM.

%	R	%	R	%	R
.01	4.0	.23	23.0	.45	37.0
.02	5.0	.24	24.0	.46	37½
.03	6.0	.25	24½	.47	38.0
.04	7.0	.26	25½	.48	38½
.05	8.0	.27	26.0	.49	39.0
.06	9.0	.28	26½	.50	39½
.07	10.0	.29	27½	.51	40½
.08	11.0	.30	28½	.52	41.0
.09	12.0	.31	28½	.53	41½
.10	13.0	.32	29½	.54	42.0
.11	14.0	.33	30.0	.55	42½
.12	14½	.34	30½	.56	43.0
.13	15½	.35	31.0	.57	43½
.14	16.0	.36	31½	.58	44.0
.15	16½	.37	32.0	.59	44½
.16	17½	.38	32½	.60	45.0
.17	18½	.39	33½	.61	45½
.18	19.0	.40	34.0	.62	46.0
.19	20.0	.41	34½	.63	46½
.20	20½	.42	35½	.64	47.0
.21	21½	.43	36.0	.65	47½
.22	22½	.44	36½		

#### METHODS EMPLOYING PRELIMINARY SEPARATION WITH CUPFERRON

The following procedure, though especially designed for stainless and heat-resistant steels, has been written to provide for the determination of titanium in any steel, which fact accounts for its apparent lengthi-

ness. When the steels to be analyzed are of known composition, it may be shortened somewhat, and is written with this object in mind. The procedure also provides for the determination of the titanium colorimetrically, gravimetrically, or volumetrically. Reasons for many of the steps have been given in the introduction under *Methods Available*.

### Weight of Sample

If titanium is under 1 per cent but over 0.05 per cent and is to be determined by color, use 0.5 g of sample, but if it is to be determined gravimetrically or volumetrically, use 1 g. For very small percentages of titanium, under 0.10 per cent, use 2.5 to 5 g. If the titanium present exceeds 1 per cent, use 1 g of sample and determine it gravimetrically or volumetrically.

### Special Solution Required

**Cupferron (6-per cent).**—Dissolve 2 g of ammonium nitrosophenylhydroxylamine ( $C_6H_5N \cdot NO \cdot ONH_4$ ) in 35 ml of cold water, and use at once.

### Procedure

**Solution of Sample and Treatment of Residue.**—Transfer the sample to a 200-ml beaker, add 100 ml of a 10-per cent solution of sulphuric acid and heat until all action appears to have ceased. (Some chemists add the acid in proportion to the sample—50 ml for 0.5 g and 150 for 5 g.) If the solution is clear or the residue is slight, proceed as directed below for the separation with cupferron.

If the residue is large, indicating much copper, or tungsten, chromium or vanadium, stir in 1 or 2 ml of ammonium sulphide, filter, wash the residue well with hot dilute sulphuric acid (1:10), boil the filtrate to expel  $H_2S$ , and proceed as directed in (a) or (b) below.

(a) Cool the filtrate and continue as directed below for the separation with cupferron. Transfer the paper and acid insoluble residue to a 200-ml beaker, add 15 ml of water and 10 ml of nitric acid, and heat till the copper sulphide has dissolved. Dilute with 50 ml of water, add an excess of ammonia, heat to boiling, and filter. Wash the filter with hot water, burn the paper at as low a temperature as possible, and add the residue to the ignited cupferron precipitate obtained from the original filtrate.

(b) Transfer the residue to a crucible and ignite uncovered at a temperature just sufficient to burn the paper. Fuse with a little  $Na_2CO_3$ , leach the melt with hot water, and filter. Dissolve the residue with hot dilute  $HCl$  (1:1), wash the paper with water, add an excess of ammonia, and filter. Ignite gently, fuse with a little  $NaHSO_4$ , and add to the original filtrate.

**Separation with Cupferron.**—Cool the solution to  $10^\circ C$ , stir in a little ashless paper pulp, and precipitate titanium, vanadium, zirco-

mium, etc., with a little of the iron by adding, dropwise, 10 ml of a 6-per cent freshly prepared solution of cupferron (ammonium nitroso-phenylhydroxylamine,  $C_6H_5N \cdot NO \cdot ONH_4$ ), stirring constantly until the precipitate assumes a reddish brown color. Fill the tip of a close 11-cm filter paper with a little ashless paper pulp, filter, and wash the precipitate 5 times with cold dilute sulphuric acid (5-per cent).

In the absence of vanadium, and if it is desired to determine Ti in  $H_2SO_4$  solution, transfer the filter and precipitate to a 50-ml platinum crucible and ignite at a temperature no higher than necessary to destroy the paper. Cool, add about 1 g of potassium pyrosulphate,  $K_2S_2O_7$ , fuse gently, and dissolve the melt in 50 ml of dilute sulphuric acid (1:4). Cool the solution to room temperature and determine titanium colorimetrically as directed in a succeeding section.

In the presence of vanadium, and if it is desired to determine Ti in  $H_2SO_4$  solution, transfer the residue remaining after igniting the cupferron precipitate to a large platinum crucible, or, preferably, to a 100-ml platinum dish. Add 5 ml of hydrofluoric acid (48-per cent), 10 ml of perchloric acid (70-per cent), and evaporate to a volume under 5 ml. Cool, dilute to 50 ml, neutralize with NaOH solution (10-per cent), and add 5 ml in excess. Boil 5 to 10 minutes, and when the precipitate, which contains the titanium, has settled, filter it off upon a close paper, and wash it with hot water. Ignite the paper and residue gently, fuse with a little potassium pyrosulphate ( $K_2S_2O_7$ ), and complete the determination by color as directed later for sulphuric acid solutions.

In the presence of vanadium, or if it is desired to determine titanium by color in perchloric acid solution, transfer the paper containing the cupferron precipitate to the original beaker. Add 50 ml of nitric acid, insert a stirring rod, cover the beaker, and evaporate rapidly to about 15 ml. Push the cover glass to one side and cautiously add 5 ml or 10 ml (according to the amount of sample used) of 60-per cent perchloric acid. Evaporate rapidly until dense fumes of perchloric acid are condensing on the wall of the beaker, and continue the fuming for 3 minutes. Cool rapidly, rinse the cover glass and the inner surface of the beaker with water, dilute to about 25 ml, and heat gently until salts are in solution.

If much copper is present, it can be removed at this stage by diluting to 100 ml, passing  $H_2S$ , filtering, washing with water, and boiling down the filtrate and washings to 25 ml.

To remove vanadium, carefully add sodium peroxide to the hot solution, stirring vigorously, until the solution is neutral, then add 1 g in excess and boil for 5 minutes, to decompose the peroxide, which would hold some of the titanium in solution. Stir in a little paper pulp and filter off the precipitate, which contains the titanium and the small amount of iron precipitated by the cupferron. Wash 5 times with hot

water and transfer the paper and precipitate to the original beaker. Add 5 ml of nitric acid and 10 ml of perchloric acid (60-per cent). Then, evaporate to fumes of perchloric acid as before to destroy the paper and drive off nitric acid, and complete the determination as described below.

### Determination of the Titanium by Color

**In Perchloric Acid Solution.**—In a beaker of the same color of glass, prepare a blank consisting of the same volumes of water and perchloric acid as the sample, add 5 ml of 3-per cent hydrogen peroxide, and then just enough of the standard titanium perchlorate solution to match the color of the sample, which usually has a slight yellowish tinge due to a little ferric iron. Cool the solution of the sample to the same temperature as the blank, add 5 ml of 3-per cent hydrogen peroxide, and dilute to a volume that will give a depth of color suitable for comparison. Transfer the solution to comparison tubes, dilute the blank to the same volume, and add standard titanium perchlorate solution and the same volume of water to the sample until the colors match. Multiply the ml of the standard solution required to match the color of the sample by its titanium value times 100 and divide by the weight of sample used to find the per cent vanadium.

**In Sulphuric Acid Solution.**—Transfer the solution, which should not contain more than 0.005 g of titanium (0.5 per cent on 1-g sample, or 1 per cent on 0.5-g sample), to a color comparison tube. Add 5 ml of 3-per cent hydrogen peroxide ("dioxygen") and mix thoroughly. To another comparison tube add 45 ml of cold 10-per cent  $\text{H}_2\text{SO}_4$ , 5 ml of the same hydrogen peroxide solution, and then add from an accurate burette measured amounts of standard titanium sulphate solution (1 ml = 0.0005 g Ti), mixing after each addition, until the color of the standard is slightly less intense than the solution. Dilute the standard to the same volume as the unknown and mix. After preliminary comparison, add titanium sulphate solution to the standard, adding at the same time an equal volume of 10-per cent  $\text{H}_2\text{SO}_4$  solution to the unknown, and mixing after each addition, until the colors match exactly. To find the per cent titanium in the sample, multiply the number of ml of standard titanium sulphate solution used by 0.05 and divide by the weight of sample taken.

## GRAVIMETRIC AND VOLUMETRIC METHODS

### The Cupferron-Ammonium Sulphide Method (Procedure of T. R. Cunningham, slightly modified)

In this method cupferron is used for both the initial and the final separation of titanium with intermediate sulphide separations to remove contaminants of the cupferron precipitate. Following the final precipitation, the titanium may be determined gravimetrically, volu-

metrically, or colorimetrically. The method may be applied to any steel or alloy of iron, containing little or much titanium, by controlling the size of sample used for analysis.

**Weight of Sample.**—For all steels to which titanium is added, use 1 g of sample; for little titanium, as in carbon steels, use 5 g of sample. For alloys containing much titanium, use 0.5 g or 0.25 g of sample.

**Procedure.**—Treat 1 g of the sample for the separation of titanium with cupferron as directed for the color methods above. Also, see *Chemical Separations, Separations with Cupferron*. Ignite the precipitate in a 100-ml platinum dish at a temperature just sufficient to burn the paper completely. Cool, and to remove silica, add 15 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) and 10 ml of hydrofluoric acid (48-per cent), then evaporate in an air bath to fumes. Rinse down the wall of the dish with cold water and again evaporate to fumes to expel every trace of HF. Add 50 ml of water and filter. Wash the residue with hot water and reserve the filtrate.

Ignite the residue at low temperature in a platinum crucible and fuse with a little potassium pyrosulphate or borax glass. Take up in cold, dilute  $\text{H}_2\text{SO}_4$  (1:4), add a slight excess of ammonia, and heat to boiling. Filter, if there is a precipitate, and wash with hot water. Dissolve the precipitate with a little hot dilute  $\text{H}_2\text{SO}_4$  (1:3), and add to the reserved filtrate.

To remove copper, cobalt, iron, nickel, etc., add to the solution, which contains all the titanium, 1 g of tartaric acid, make slightly ammoniacal, neutralize with dilute  $\text{H}_2\text{SO}_4$ , and add an excess of 2 ml of the concentrated acid for each 100 ml of solution. Saturate the solution with  $\text{H}_2\text{S}$  and separate any precipitate by filtering and washing thoroughly with  $\text{H}_2\text{S}$  water containing about 1 per cent of  $\text{H}_2\text{SO}_4$  and 1 per cent of tartaric acid. Discard the precipitate. Now add to the solution ammonium hydroxide until there is an excess of 2 ml per 100 ml of solution, and pass  $\text{H}_2\text{S}$  for 5 minutes. Stir in some ashless paper pulp and filter. Wash the precipitate well with ammonium sulphide containing about 1 per cent ammonium tartrate and discard it. Boil the filtrate to the complete expulsion of  $\text{H}_2\text{S}$ .

Adjust the volume of the solution to 150 ml and add 30 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1). Cool to  $10^\circ\text{C}$ , add some paper pulp, and precipitate titanium with cupferron as directed above, adding the cupferron until there is an excess as indicated by the formation of a snow-white precipitate which rapidly disappears. Filter, wash 12 to 15 times with cold 5-per cent  $\text{H}_2\text{SO}_4$ , and then 5 times with 5-per cent ammonium hydroxide. Transfer the paper and precipitate to a platinum crucible and gradually ignite to between  $1050^\circ$  and  $1100^\circ\text{C}$ . Cool in a desiccator and weigh. Multiply the weight of the  $\text{TiO}_2$  thus found by 59.95 and divide by the weight of sample taken to find the percentage of titanium.



To check the results, fuse with potassium pyrosulphate, take up in dilute  $\text{H}_2\text{SO}_4$  (6-per cent), and proceed by one of the following methods:

(a) Pass the solution through a Jones reductor into a mixture of ferric sulphate and phosphoric acid, and titrate with 0.05 *N*  $\text{KMnO}_4$  solution. Make a blank determination in the same way and correct. One ml of 0.05 *N*  $\text{KMnO}_4 = 0.002395$  g Ti.

(b) Aliquot the solution and determine titanium in a suitable portion colorimetrically. If results do not check, test for other elements, such as zirconium, and correct the titanium gravimetric result.

### Umpire Method for Titanium in Steels<sup>1</sup> Using the Thiosulphate-Phenylhydrazine Method of Separation

**Principles of the Method.**—This method, in which the titanium is determined gravimetrically as  $\text{TiO}_2$ , originally depended upon the precipitation of the titanium by hydrolysis in slightly acid solution with sodium thiosulphate (sodium hyposulphite),  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . With the thiosulphate alone, traces of aluminum, chromium, iron, and vanadium are carried down with the titanium, and if zirconium is present, the precipitation of the titanium is incomplete. The latter drawback is overcome by adding phenylhydrazine,  $\text{C}_6\text{H}_5\text{HN} \cdot \text{NH}_2$ , a poisonous compound obtained as an oily liquid at the higher room temperatures. Elements completely precipitated by phenylhydrazine include aluminum, titanium, zirconium, thorium, and chromium; also phosphorus and vanadium, if the former elements are present in considerable proportions. Elements partly precipitated include Be, Ce, Cd, Co, Fe, Hg, Ni, and Zn, the amount precipitated varying with the concentration. Hence, the initial precipitation must be followed by appropriate separations to obtain the  $\text{TiO}_2$  in a form sufficiently pure for weighing. In the following method titanium and zirconium are separated by fusing the first precipitate with  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$  and purifying by a reprecipitation with  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , followed by a final treatment with  $\text{NH}_4\text{OH}$  and KCN. The combined oxides of Ti and Zr are weighed, the latter is separated as phosphate, and the  $\text{TiO}_2$  obtained by difference.

**Procedure.**—Transfer 2 to 5 g (depending upon the Ti present) of the sample to a 400-ml beaker and dissolve with 100 ml of dilute HCl (1:1). In the absence of tungsten, much chromium, molybdenum, or vanadium, dilute the solution to 300 ml, make slightly alkaline with  $\text{NH}_4\text{OH}$ , just acidify with HCl, add 3 ml in excess, then 5 g of sodium thiosulphate dissolved in 10 ml of water, boil for 10 minutes, and proceed as directed in the second paragraph below.

In the presence of tungsten, or if a considerable residue remains insoluble in HCl, add 100 ml of water containing 3 g of sodium chlorate,  $\text{NaClO}_3$ , and boil until the residue is dissolved and until tungsten, if present, has been converted to the yellow tungstic acid.

Filter, wash with dilute HCl (1:10), and reserve the filtrate. With a fine jet of water, sluice any tungstic acid into the original beaker; dissolve with 5 ml of  $\text{NH}_4\text{OH}$ . Wash the filter with dilute ammonia (1:10), filter off any insoluble residue through the same paper, wash as before, and discard the filtrate. Ignite the paper and transfer the ash to the reserved filtrate. Dilute to 260 ml, make slightly alkaline with ammonia, and add 3 ml of HCl in excess of the neutral point. Add 50 ml of water containing 25 g of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , boil for 10 minutes, and proceed as directed below.

Add to the reduced solution 3 ml of phenylhydrazine, stir in a little paper pulp, and boil for 5 minutes. Filter and wash the precipitate 5 times with 20-25 ml portions of hot water, and ignite it under good oxidizing conditions in a clean platinum crucible. Add to the crucible 3 g of  $\text{Na}_2\text{CO}_3$  and a few crystals of  $\text{NaNO}_3$  (not  $\text{KNO}_3$ ), mix with a platinum rod, and fuse the contents until the melt is clear. Transfer the fusion to a 150-ml beaker and clean the crucible thoroughly with hot water, adding in all 50 to 60 ml. Boil the contents of the beaker until disintegration of the melt is complete, filter the solution, and wash the residue thoroughly with hot water, discarding the filtrate.

If the amount of titanium present does not exceed 0.01 g and the analysis is routine, boil the residue and paper for 10 minutes in 50 ml of dilute sulphuric acid (1:1), filter, wash with water, and complete the determination as directed under the color methods, using the titanium sulphate standard.

In referee work or special investigations, dissolve the residue in 10 ml of hot dilute HCl (1:1), wash the paper with hot water, and reserve both the solution and the paper for treatment as follows:

To the solution add ammonia until it is slightly alkaline, then HCl until it is slightly acid, and stir in 1 g of sodium thiosulphate. Heat the solution until all ferric iron present is reduced, as indicated by the drop test with KCNS, and add 5 ml of ammonia containing 1 g of potassium cyanide to hold the ferrous iron in solution. Boil for 1 minute, add the reserved paper, macerate it thoroughly, and filter. Wash the beaker, filter and precipitate with water to which a few drops of ammonia have been added, and transfer the paper to a weighed platinum crucible. Dry the paper, ignite at a low temperature till the paper is consumed, then at  $1200^\circ\text{C}$ . Cool and weigh as  $\text{TiO}_2 + \text{ZrO}_2 + \text{Ta}_2\text{O}_5 + \text{SiO}_2$ . Add 1 or 2 drops of dilute sulphuric acid (1:1), evaporate with hydrofluoric acid, ignite, and reweigh as  $\text{TiO}_2$  if Zr and Ta are known to be absent.

If there is doubt concerning the presence of Zr or Ta, fuse the ignited residue with a little  $\text{K}_2\text{S}_2\text{O}_7$  or borax glass. Also fuse a blank test, using the same amount of the flux. Dissolve the melts separately in cold dilute sulphuric acid (1:10), and determine the titanium colorimetrically, using the standard titanium sulphate solution.

As the solution used in the colorimetric determination contains all the zirconium in the sample, it may be used to advantage not only for checking the colorimetric result for titanium, but also for the determination of zirconium. To this end, add 0.5 g of diammonium phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ , and allow the solution to stand 10 hours or longer at a temperature between 50 and 60° C, adding a little hydrogen peroxide occasionally to maintain a moderate excess at all times. Filter, wash with a 5-per cent solution of ammonium nitrate and weigh as  $\text{ZrP}_2\text{O}_7$ . Fuse with  $\text{K}_2\text{S}_2\text{O}_7$  as before and repeat the precipitation. Multiply the weight of the  $\text{ZrP}_2\text{O}_7$  by 46.45 and subtract from the combined weights to find the weight of  $\text{TiO}_2$ . Multiply the weight of  $\text{TiO}_2$  by 59.95 and divide by the weight of sample used to find the per cent titanium in the sample.

The weight of  $\text{ZrP}_2\text{O}_7$  multiplied by 34.389 and divided by the weight of sample used gives the per cent zirconium, which may be contaminated with tantalum if it is present. Unless tantalum is known to be present, or there is reason to suspect its presence, it may be considered as absent, and the result reported as per cent Zr.

#### Text Reference

1. "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Alloy Steels," second edition, and "Chemical Analysis of Iron and Steel," Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., New York, John Wiley and Sons, Inc., 1937.

# Determination of Aluminum.

## Methods Available

A small proportion of aluminum in some form may be found in any steel, even though no metallic aluminum is added in its manufacture. In steels to which it is added, the proportion found in the finished steel will vary from 0.005 per cent to 1 per cent and more. The first problem, therefore, is the separation of the aluminum from the large percentages of iron present.

One of the early methods for making this separation was the phosphate method in which the Al is precipitated with ammonium phosphate in slightly acid reduced solution buffered with ammonium acetate, along with all the Cb, Sn, Ta, Zn, Zr, most, if not all of the Cr and V, and some of the Cu and Ni, if these elements are present, and a little of the iron. Various modifications of this method have been developed to adapt it to the numerous alloy steels, but one precaution generally overlooked is that for the separation of tin, which has become a common component of steels. Other methods of separation are:

(1) The Ether Extraction Method, which leaves the Al associated with all or a part of all other elements present, except  $\text{Fe}^{\text{iii}}$  and Mo.

(2) Precipitation with Sodium Bicarbonate, which throws down Al with Cr, Cb, Cu, P, Sn, Ti, Ta, U, V, W, Zr, and any ferric iron present.

(3) Precipitation with Phenylhydrazine, which precipitates Al,  $\text{Fe}^{\text{ii}}$ , Cr, V, Ti, Zr.

(4) Precipitation with 8-Hydroxyquinoline, which separates Al from As, Be, Bo, Cb, Cr, F, Mo, P, Ta, Ti, V, and W, has been made use of as a secondary separation.

Other methods, which, although the separations are complete, are not so suitable for separating large percentages of iron, are:

(5) Electrolysis over a mercury cathode which throws into the mercury Fe, Mn, Cr, Zn, Ni, Cu, Sb, Sn, Mo, and Co, and leaves in solution Al, As, B, Be, Cb, P, Ta, Ti, U, V, W, and Zr. Large proportions of Fe and Cr decrease the fluidity of the mercury and make it awkward to handle.

(6) Precipitation with Cupferron, which precipitates  $\text{Fe}^{\text{iii}}$ , Cu, Sn, V, Ti, Zr, Cb, Ta, and  $\text{U}^{\text{iv}}$ . If the precipitation is made in reduced solution and precautions taken to see that all of the iron is reduced, a separation of these elements with very little iron accompanying them can be made.

(7) And Precipitation with Ammonium Sulphide in dilute tartaric

or nitric acid solution, which precipitates Co, Fe, and Ni, leaving other elements in solution.

### **Total Aluminum, Metallic Aluminum, and $\text{Al}_2\text{O}_3$ in Steel**

Aluminum occurs in steel as metallic aluminum alloyed with iron, and as compounds, such as alumina, aluminum silicates, aluminum ferrites, and, more rarely, perhaps, as aluminum nitrides. Small as well as large percentages of aluminum are capable of affecting markedly the properties of the steel, and it has been a question as to whether or not some of these effects are due to the metallic alloyed aluminum or to one or more of its finely dispersed compounds. Another problem, therefore, has been the separation and determination of the metallic aluminum and of the combined aluminum, a problem upon which much effort has been expended and for the solution of which many methods have been proposed; but all have failed to give results not open to question as to their accuracy or as to whether or not they represented metallic alloyed or combined aluminum. Included in the methods that follow is one, which, as indicated by our research, will give a fairly accurate separation of  $\text{Al}_2\text{O}_3$  from the metallic aluminum in carbon steels and leaves no question as to the accuracy of the results on solutions obtained in the initial separation.

## **METHODS FOR THE DETERMINATION OF TOTAL ALUMINUM IN STEEL**

### **Method Using the Bicarbonate Separation**

#### **Application of the Method**

The following method is applicable to the determination of large or small percentages of aluminum in any steel, except steels containing tungsten. Also, it should serve admirably for the separation and determination of titanium, columbium, tantalum, zirconium, chromium, and possibly, uranium. Both aluminum and titanium have been determined in the same sample by this method with satisfactory results. The separations as outlined have one advantage besides the fact that they are complete, in that they make it possible for the analyst to detect the presence of interfering elements as the analysis progresses. For instance, one group contains titanium, columbium, tantalum, zirconium, and vanadium, and a precipitate at this point shows that at least one of these elements is present. It then remains for the analyst to determine which element it is, or to separate them if there are more than one. It should be possible also to determine chromium in the filtrate after the final separation of aluminum. Hence, the method is especially adapted to the analysis of unknown steels.

#### **Weight of Sample**

The weight of sample is varied according to the percentage of aluminum present as follows:

For carbon steels, use 10 g of sample.

For low-aluminum steels, use 2 g of sample.

For high-aluminum (1 to 5 per cent), use 1 g of sample.

### Special Solutions

**Cupferron Solution (6-per cent).**—Dissolve 2 g in 35 ml of water. Cool and use fresh.

**Blanks.**—As a check on reagents, which may contain traces of aluminum, a blank test is carried along with each analysis, and in the most exacting analyses a standard sample of steel should also be run through in parallel with the blank and each lot of samples.

### Procedure

**Solution of Sample and Separation with Bicarbonate.**—Weigh 10 g of steel in a 500-ml Erlenmeyer flask, add 100 ml of water and 11 ml of sulphuric acid. Cover the flask with a small watch glass and keep near the boiling point till all the steel is in solution. Add 100 ml of hot water, containing 1 to 2 g of sodium sulphite, heat to boiling, and boil till the odor of  $\text{SO}_2$  becomes faint. Add an 8-per cent solution of sodium bicarbonate, from a burette, till a slight permanent precipitate forms, then add 6 ml in excess. Heat to boiling and boil for 1 minute. As soon as the precipitate has settled, filter, and wash several times with hot water.

The precipitate should contain all the aluminum, chromium, titanium, tin, columbium, tantalum, uranium, zirconium, probably all of the vanadium, and most of the copper. These elements may be separated and aluminum recovered by two methods as follows:

**A. NaOH Separation.**—Dissolve the precipitate from the paper with 20 ml of hot dilute HCl (1:3) and wash well with hot water. Ignite the paper and any residue in a platinum crucible and fuse with sodium or potassium pyrosulphate. Dissolve the fusion in the HCl solution. Add 2 ml of  $\text{H}_2\text{SO}_4$  and boil for 2 to 3 minutes. Add 2 to 3 ml  $\text{HNO}_3$  (sp. gr. 1.42) and boil 2 to 3 minutes more. Nearly neutralize the acid solution with NaOH and pour slowly and with constant stirring into 80 ml of a 5-per cent solution of NaOH. Allow the precipitate to settle and filter the solution, which contains Al,  $\text{Cr}^{\text{vi}}$ , Mo, P, and V, through a close filter paper and wash the filter several times with a 1-per cent solution of NaOH. Acidify the filtrate with HCl, adjust the volume to 250 ml, and determine Al by the phosphate method, unless Cr, Mo, or V is present, in which case proceed as follows:

**B. Separation of Cu, Fe, Mo, Sn, and Co as Sulphides.**—Dissolve the bicarbonate precipitate off the paper with hot 1-1 hydrochloric acid into the flask in which the precipitation was made. Place the flask on a hot plate and boil till all of the soluble matter has dissolved. Place a 400-ml beaker under the funnel and pour the solution from

the flask through the paper, making sure that all of the insoluble matter is transferred to the paper. Wash with hot water. Burn the paper and insoluble matter in a platinum crucible and fuse with sodium pyrosulphate. Dissolve the fusion in the filtrate.

Add ammonia to the solution drop by drop till a permanent precipitate forms and then add 5 ml of hydrochloric acid. Dilute to 250 ml and heat to boiling and pass a current of hydrogen sulphide through the solution for about 20 minutes while it is cooling. Filter off the sulphide precipitate and wash with 2-per cent hydrochloric acid saturated with hydrogen sulphide. If desired, reserve the precipitate, which contains the copper, tin, and molybdenum, for the determination of these elements.

Add 2 g of tartaric acid to the filtrate, neutralize with ammonia, and add 10 ml in excess. Pass a current of hydrogen sulphide through this solution for 20 minutes, let settle, and filter. Wash with ammonium sulphide containing tartrate. Discard the precipitate containing the iron and cobalt, if the latter is present, and reserve the filtrate which contains all of the aluminum, columbium, tantalum, vanadium, and zirconium.

**Separation with Cupferron.**—Boil the filtrate to expel ammonium sulphide, dilute to 250 ml, add 25 ml of hydrochloric acid, and again boil to expel the last traces of hydrogen sulphide. Cool in ice water and add potassium permanganate solution till a pink color persists for one-half minute. To the cold solution, add a 6-per cent solution of cupferron drop by drop till no more precipitate forms. Filter, using paper pulp, and wash with cold water containing 100 ml of hydrochloric acid and 0.5 g of cupferron to the liter. If desired, reserve the precipitate, which contains the titanium, columbium, tantalum, vanadium, and zirconium, and treat the filtrate, which contains the aluminum and chromium, as follows:

**Separation of Aluminum with Ammonia.**—Add 25 ml of sulphuric acid and 40 ml of nitric acid to the filtrate and boil down to incipient fumes on a hot plate. Cool, rinse the watch glass and wall of the beaker, add 30 ml of nitric acid, and again evaporate to incipient fumes. Repeat this operation as often as necessary to oxidize all of the organic matter. When all the organic matter has been oxidized, cool the solution, dilute to 150 ml, filter off the silica, and wash well with hot 3-per cent sulphuric acid. Add 3 drops of methyl red to the filtrate and ammonia drop by drop till a distinct yellow color appears. Heat to boiling, boil for 1 minute, and filter, washing with hot water containing ammonium nitrate. Dissolve the precipitate off the paper into a 400-ml beaker with hot dilute hydrochloric acid (1:1) and wash the paper well. Add 15 to 20 ml of perchloric acid to the solution and boil till the chromium appears to be oxidized, and then boil 10 minutes longer. Cool, dilute to 200 ml with water, and neutralize

with ammonia, using the chromium, if present, as an indicator. If no chromium is present, add methyl red indicator before adding ammonia. Heat to boiling and boil for 1 minute. Filter and wash the precipitate, which contains the aluminum and phosphorus, with hot water containing ammonium nitrate. Dissolve the precipitate with hot dilute hydrochloric acid (1:1) and wash the paper thoroughly with hot water, or macerate it in the acid.

**Determination of Aluminum as Phosphate.**—Dilute the acidified solution, if necessary, to a volume of 250 ml, and add 0.5 g of diammonium phosphate. Add a little macerated paper, if the paper was not macerated, and 2 drops of methyl red indicator, then make just ammoniacal. Restore the pink color with several drops of dilute HCl (1:20). Heat the solution to boiling and add 20 ml of a 25-per cent solution of ammonium acetate. Continue the boiling for 5 minutes, allow to settle, or digest for 1 or 2 hours for small proportions of aluminum, filter on a 9-cm No. 42 Whatman or similar paper, and wash with hot 5-per cent ammonium nitrate until 5 ml of the washings no longer give a test for chlorides with acidified silver nitrate. Ignite gradually in an open platinum or porcelain crucible, until constant weight is obtained, and weigh as  $\text{AlPO}_4$ . Multiply this weight by 0.221 to find the weight of aluminum, which is multiplied by 100 and divided by the weight of sample taken to find the per cent aluminum in the sample.

### Method Using the Ether Separation

#### Solution of Sample

Dissolve 10 g of the steel in 200 ml of dilute hydrochloric acid (1:1). When in solution, heat to boiling and oxidize with nitric acid, using just enough to oxidize the iron completely. Boil to expel nitrous fumes, filter through an 11-cm filter paper, and wash with hot dilute hydrochloric acid (1:1) and hot water. Retain the precipitate.

#### Separation of $\text{Fe}^{\text{III}}$ with Ether

Evaporate the filtrate to a syrupy consistency and make an ether separation according to the procedure outlined under *Chemical Separations*. Treat the acid solution from the ether separation, which contains all of the aluminum and chromium excepting the insoluble oxides and carbides that were retained on the filter paper, as follows:

#### Oxidation of Chromium and Separation with Ammonia

Make sure that all ether or other organic matter has been expelled, then add 60 ml of perchloric acid (68- to 70-per cent) to the acid solution and boil till the solution has become concentrated and all the chromium has been oxidized, which may require heating for 1 to 5 minutes after the fuming stage is reached. Cool, dilute to 200 ml with hot water, and stir till the salts are completely dissolved. Precipitate



the iron and aluminum with ammonium hydroxide, exercising great care to avoid adding an excess of ammonia. If red litmus paper is used as an indicator, stop the addition of ammonia as soon as the paper has a slightly blue tinge. Boil for a few minutes, filter on an 11-cm filter paper, and wash with a hot 2-per cent solution of ammonium nitrate. To insure complete removal of chromium, make a second separation by dissolving the precipitate off the paper with hot HCl (1:2), adding 20 ml of perchloric acid, proceeding as in the first precipitation, and filtering through the same paper.

Dissolve the precipitate on the paper, which contains all of the aluminum that was in solution, plus iron, titanium, etc., into a 400-ml beaker with hot hydrochloric acid (1:1), and wash the paper with hot water. Place the paper together with the paper from the original filtration in a platinum crucible, burn off the paper, and fuse the contents of the crucible with sodium pyrosulphate. Dissolve the fusion in the acid solution contained in the 400-ml beaker. When the fusion has completely dissolved, rinse the crucible, and add ammonium hydroxide to the solution till a slight permanent precipitate forms. Now add 2 ml of hydrochloric acid which will completely dissolve the precipitate, adjust the volume of the solution to about 200 ml, and add 2 g of tartaric acid. Complete the determination as directed in the preceding method, separating Cu, Fe, Mo, Sn, and Co as sulphides, Cb, Ta, Ti, V, and Zr with cupferron, Al and P from Cr with ammonia following oxidation with perchloric acid, and finally precipitating Al as phosphate.

### The Phosphate Method

This method is best adapted to carbon and low-alloy steels. Applied to steels containing much chromium, it is troublesome, and is lacking in accuracy when applied to steels containing much aluminum, say over 1 per cent. When properly applied and carried out, it has given satisfactory results, but is long and tedious. It has one advantage in that it requires no special separation of phosphorus.

### Weight of Sample

For carbon and other steels, except tungsten steels, containing less than 0.10 per cent aluminum, use 5, 10, or 20 grams according to the accuracy desired. For higher aluminum reduce the weight of sample according to the percentage present, using 1 g for 1 per cent aluminum. For high-tungsten steels, 2 to 3 g of sample are all that can be treated conveniently.

### Blank Test

A blank test, preferably a standard sample of steel on which Al has been accurately determined, should be analyzed in parallel with each determination.

### Procedure

**Solution of Sample.**—*Presence of Tungsten.*—Weigh 2 portions of  $2\frac{1}{2}$  g each, transfer to separate 250-ml beakers, and dissolve with 50 ml of HCl (1:1). Heat and add  $\text{HNO}_3$ , dropwise, till the  $\text{H}_2\text{WO}_4$  is a bright yellow, then add 5 ml excess and digest to decompose carbides. Dilute somewhat, filter, and wash 2 or 3 times with hot water. Evaporate the filtrate to near dryness and treat with HCl to expel  $\text{HNO}_3$ . Reduce the solution with  $\text{SO}_2$ , boil off the excess, and treat as directed below for the separation of Al with phosphate. Dissolve the tungsten on the filter with dilute ammonia (1:5), wash with water, and reserve the filter to be ignited with the first phosphate precipitate.

*Absence of Tungsten.*—Dissolve the sample in 75 to 150 ml of  $\text{H}_2\text{SO}_4$  (1:9) contained in a 600- to 800-ml beaker, heating gently. Dilute, filter, wash with water, and reserve the filter for ignition with the impure phosphate, if total aluminum is required.

To eliminate As, Cu, Sn, Mo, etc., heat to  $60^\circ\text{C}$ , saturate with  $\text{H}_2\text{S}$ , digest 30 minutes, filter, wash with dilute acid, and discard the precipitate. Boil the filtrate to expel  $\text{H}_2\text{S}$  and treat as directed below. In the absence of these elements omit this step. Also, if preferred, delay this treatment until just before the final precipitation with phosphate.

**First Separation of Aluminum, etc., as Phosphate.**—Dilute, if necessary, to a volume of 400 ml, add 2 to 5 g of sodium phosphate, and stir in ammonia, added dropwise, until a slight precipitate is formed. Add 3 ml of dilute hydrochloric acid (1:1), sufficient (15 to 30 ml) of a 50-per cent solution of sodium thiosulphate to keep the solution reduced, and 15 ml of a 20-per cent solution of ammonium acetate. Boil 10 minutes, filter hot, and wash with hot water. Discard the filtrate. Transfer the filter and reserved paper to a platinum crucible, ignite gently, and treat by any of the following methods to remove chromium, titanium, etc.

**Separation of Cr, Ti, etc.**—a. Fuse with 2 or 3 g of  $\text{NaCO}_3 + 0.2$  g of  $\text{NaNO}_3$ , leach with water, filter, wash 1 or 2 times with water, reserve filtrate, ignite the filter, and repeat the treatment, combining the filtrates and washings. Discard the residue, acidify the filtrates with HCl, boil to expel  $\text{CO}_2$ , and treat as directed below for the final precipitation of the alumina.

✓ b. Fuse the impure phosphate with a little  $\text{K}_2\text{S}_2\text{O}_7$ . Dissolve in hot water, add  $\text{Na}_2\text{O}_2$ , and boil to oxidize chromium, etc. Filter, add  $\text{Na}_2\text{O}_2$ , boil, and filter again. Acidify the combined filtrates with  $\text{H}_2\text{SO}_4$ , boil, and add ammonia carefully till red litmus barely changes to blue. Boil, filter, and wash with hot water. Dissolve the precipitate with hot, dilute HCl (1:10), and wash the paper thoroughly with hot water.

c. If only chromium is to be eliminated, dissolve the gently ignited

phosphate precipitate with 10 ml of  $\text{HClO}_4$ , and fume for 15 minutes. Dilute, precipitate Al with ammonia, filter, wash, and redissolve as directed above.

If desirable, purify by treating with  $\text{H}_2\text{S}$  at this point.

**Final Precipitation as Phosphate.**—Adjust the volume of the acidified filtrate to 250 ml, and add 0.5 to 1 g of  $(\text{NH}_4)_2\text{HPO}_4$ . Add 2 drops of methyl red indicator, and add dilute ammonia slowly till the color just changes. Stir in dilute  $\text{HCl}$  (1:20) till the color changes to red again. Add 20 ml of a 20-per cent solution of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , boil 5 minutes, and let the precipitate settle 1 to 2 hours for very small percentages of aluminum. Filter, wash once or twice with water, and dissolve with  $\text{HCl}$  and reprecipitate, if the sample contains vanadium. After the last filtration, wash with 5-per cent solution of  $\text{NH}_4\text{NO}_3$  until the washings give no test with  $\text{AgNO}_3$  for chlorides. Ignite gradually to  $1000^\circ\text{C}$  for 2 and one-half hours. Cool and weigh as  $\text{AlPO}_4$ . Subtract the blank, multiply the difference by 22.11, and divide by the weight of sample used to find the per cent aluminum. To test for vanadium, dissolve the ignited precipitate in dilute  $\text{HNO}_3$ , and add  $\text{H}_2\text{O}_2$ , noting if any signs of a straw color are developed.

#### METHODS FOR DETERMINATION OF METALLIC ALUMINUM AND ALUMINUM OXIDE

In our research work on this subject, we have studied and compared the various acid solution methods as well as the latest electrolytic solution methods of Herty and Fitterer and of Benedicks. On the whole, and with respect to  $\text{Al}_2\text{O}_3$ , results by the acid solution methods compare favorably with results by the electrolytic methods, and are much simpler. Regarding the accuracy of the former, we have been able to establish only that the  $\text{Al}_2\text{O}_3$  results obtained by solution in dilute nitric acid are slightly higher than results by solution in other acids, and about the same as results obtained by solution in dilute sulphuric acid (1:9), which are generally higher than the  $\text{Al}_2\text{O}_3$  obtained by dissolving in perchloric acid, and always higher than with hydrochloric acid. Other factors affecting the reproducibility of results are the temperature of solution, the time of standing after solution is effected, indicating the  $\text{Al}_2\text{O}_3$  is slowly dissolved, and the closeness of the paper used in filtering. The best conditions are given in the following methods which are based on these studies and designed especially for application to carbon steels.

#### Procedures for the Determination of Insoluble Alumina

##### Weight of Sample

For carbon steels, use 10 g or 20 g, if only  $\text{Al}_2\text{O}_3$  is to be determined, of 10- to 40-mesh size drillings so that solution will be rapid.

If the filtrate is to be used for metallic aluminum, the method of separation will control the weight of sample taken, 5 g being suitable for all methods, and 10 g for bicarbonate separations.

### Solution of the Sample

Transfer the sample to a 500-ml beaker, cover, and add 10 ml of dilute  $\text{H}_2\text{SO}_4$  (10-per cent), plus 10 ml for each g of sample used. Heat gently (to  $60^\circ$  to  $70^\circ$  C) and filter rapidly through a close paper as soon as the cuttings have dissolved, washing the beaker thoroughly and the filter 3 or 4 times with dilute  $\text{H}_2\text{SO}_4$  (1:99). Reserve the filtrate for the determination of metallic aluminum, and proceed with the analysis of the residue, which may contain, besides  $\text{Al}_2\text{O}_3$ , some  $\text{SiO}_2$ , C, Cu, Cr, Mo, Cb, Sn, Ta, Ti, W, or Zr.

### Analysis of the Residue

Transfer the filter and contents to a platinum crucible and ignite gently till all carbonaceous matter is consumed. Cool, moisten the residue with 3 or 4 drops of  $\text{H}_2\text{SO}_4$  (1:1), add 3 ml of HF (48-per cent), and evaporate to dryness to eliminate  $\text{SiO}_2$ . Ignite gently and fuse with sodium pyrosulphate. Dissolve the melt in 40 ml of water containing 2 ml of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.42), and treat as follows:

### Electrolysis over Mercury Cathode

Neutralize the slightly acid solution with ammonia and add 0.2 ml of  $\text{H}_2\text{SO}_4$ . Heat, if the solution is not clear, and add 1 to 3 drops more of the acid, if necessary. Adjust the volume to 75 ml, cool, and transfer the solution to a Melaven cell, such as that described for the determination of vanadium. With about 900 g of mercury in the cell, adjust the anode to within about  $\frac{1}{4}$  inch of the surface of the mercury, and electrolyze the solution with a current of 6.3 amperes (surface area of mercury  $39.5 \text{ cm}^2$ , or  $0.16 \text{ amp per cm}^2$ ), stirring the solution constantly either mechanically or with a stream of air free of dust and foreign gases. Continue the electrolysis for at least 15 minutes, or longer, until a drop of the solution gives no test for iron when added to potassium ferricyanide indicator. Reduce the current to about 0.5 amp, dilute sufficiently or lower the platinum anode to keep it immersed till the mercury is all withdrawn, and turn the stopcock to permit the mercury to flow into a beaker. Then let the solution flow into a small beaker and rinse the empty cell with water. Filter the solution, to free it from any precipitate of manganese oxide, into a 400-ml beaker, and wash the filter with a 1-per cent solution of sulphuric acid. Complete the determination by one of the following methods:

**Precipitation of Aluminum as Phosphate.**—1. Absence of As, Cb, Sn, Ta, Ti, V, W, Zr. Add 1 or 2 drops of methyl orange indicator to the solution and 5 ml of a 10-per cent solution of ammonium phos-

phate. Neutralize with ammonia, adding a dilute solution dropwise with constant stirring until the color changes. Add 1 ml of dilute HCl (1:9) and 15 ml of a 50-per cent solution of ammonium acetate. Boil 2 minutes and allow the precipitate to settle 2 hours or longer for small proportions of aluminum. Filter with paper pulp on the filter and wash thoroughly with a warm 2-per cent solution of  $\text{NH}_4\text{NO}_3$ . Transfer the paper and contents to a weighed platinum crucible, dry, ignite gradually under most highly oxidizing conditions until the paper is burned, and then to constant weight at  $950^\circ$  to  $1000^\circ$  C. Cool and weigh as  $\text{AlPO}_4$ . Multiply by 100 times 0.4178 and divide by the weight of sample used to find the per cent  $\text{Al}_2\text{O}_3$ .

2. In the presence of As, Cb, Sn, Ta, Ti, V, W, and Zr, the procedure above must be modified as follows:

(a) To remove As and Sn, add 5-per cent  $\text{H}_2\text{SO}_4$  to the electrolyzed solution, pass  $\text{H}_2\text{S}$ , filter, boil off excess  $\text{H}_2\text{S}$ , precipitate with ammonia, and weigh as  $\text{Al}_2\text{O}_3$  or redissolve and precipitate as phosphate.

3. In the presence of small percentages of vanadium or titanium, precipitate twice with phosphate and test the final precipitate by dissolving in HCl or dilute nitric acid (for V) and adding  $\text{H}_2\text{O}_2$ . Add HF to cause color of Ti to fade.

4. In the presence of Cb, Ta, Ti, V, W, Zr, treat the electrolyzed solution for the separation and precipitation of aluminum with 8-hydroxyquinoline as directed in the following method for metallic or soluble aluminum.

### Procedures for Determination of Metallic or Soluble Alumina

#### Bicarbonate Separation Followed by Electrolysis over Mercury Cathode

This method is applicable to all steels except those containing As, Be, Cb, Ta, Ti, W, U, V, or Zr.

**Procedure.**—Dilute the original sulphuric acid solution from the  $\text{Al}_2\text{O}_3$  determination to 200 ml, heat to boiling, add 10 ml of ammonium bisulphite, and boil 5 minutes.

Proceed with the bicarbonate separation as directed under *Chemical Separations*.

Dissolve the precipitate with 100 ml of dilute  $\text{H}_2\text{SO}_4$  (10-per cent) and boil down to fumes. Ignite the filter paper gently, fuse with a little  $\text{Na}_2\text{S}_2\text{O}_7$ , dissolve in water, and use it to dilute the portion fumed with  $\text{H}_2\text{SO}_4$ . Filter to remove  $\text{SiO}_2$ , etc., wash with dilute  $\text{H}_2\text{SO}_4$  (1:99), and evaporate to about 30 ml. Cool, neutralize with dilute ammonia, add 0.2 ml  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84), then electrolyze and precipitate with ammonium phosphate as described above for  $\text{Al}_2\text{O}_3$ . Subtract any blank found and multiply by 100 times 0.2211 and divide by the weight of sample used to find the per cent of aluminum.

## Standard Procedure for Determination of Metallic or Soluble Aluminum

### Final Precipitation with 8-Hydroxyquinoline and Titration of the Aluminum Quinolate

This method is applicable to all steels, except stainless and heat-resistant steels.

The analysis is made in 3 or more steps, involving (1) solution of the sample in dilute  $\text{H}_2\text{SO}_4$ , (2) a separation with  $\text{SO}_2$  and ammonia or with  $\text{NaHCO}_3$ , (3) a separation with  $\text{NaOH}$  or electrolysis over a mercury cathode, and (4) precipitation of Al with 8-hydroxyquinoline, and (5) titration of the aluminum hydroxyquinolate with standard potassium bromate and sodium thiosulphate solutions. As  $\text{NaHCO}_3$  and  $\text{NaOH}$  generally contain traces of alumina, or tend to gather it from glassware, they are avoided by some analysts. Since the results are obtained by titrating the quinolate, they are not affected by silica gathered from glassware or chemicals. As an aid in selecting the proper separations, economizing in time, and increasing the accuracy, the following effects are to be noted.

1. Treatment with dilute sulphuric acid dissolves all the iron and most of the other elements in the steel, leaving a residue that may contain  $\text{Al}_2\text{O}_3$ , C, or carbides,  $\text{CuS}$ ,  $\text{MoS}_3$ , a little  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and compounds of Cb, Ta, Zr, W, etc. This residue is separated by filtration.

2. Treatment of the filtrate with  $\text{SO}_2$  and ammonia leaves nearly all the iron, manganese, nickel, etc., in solution, the elements precipitated depending upon the pH value. To precipitate all of the aluminum, a pH of about 4.5 must be attained and to avoid precipitating most of the iron, the alkalinity must be held under pH 5.2. In the method given below, we use methyl orange (yellow at pH 4.4) or methyl red (yellow at pH 6.2). Under the latter conditions  $\text{Fe}^{\text{iii}}$ , Cb, Zr, Ta, Sn, Ce, Th, Al, U, Zn, Cr, Cu,  $\text{Fe}^{\text{ii}}$ , Be, Ni, Co, (pH 8) will be precipitated in the order named, and other elements, such as V and As, will be carried down, depending upon the presence of others, such as phosphorus. By careful adjustment of the alkalinity, as with methyl orange, most of the Cu, Fe, Ni, Be, and Co can be left in solution.

3. In the bicarbonate separation:

The precipitate contains all of the Al, Cr, Cb, Ta, Ti, Zr, and probably all of the P, Sn, U, and V left in the filtrate.

The filtrate contains all of the Mn.

Elements that divide are Cu, Fe, Ni, Co, Sn.

Therefore, 2 and 3 are optional methods.

4. Separation with  $\text{NaOH}$ :

Precipitates: Cb, Co,  $\text{Cr}^{\text{iii}}$ , Cu, Fe, Ni, Ta, Ti, and Zr.

Leaves in Solution: Al, As,  $\text{Cr}^{\text{vi}}$ , Mo, P, Sn, V, and W.

Separation of Al is not complete if much Ni is present.

5. Electrolysis over a mercury cathode:

Drives into the mercury: Co, Cr, Cu, Fe, Mo, Ni, Sb, Sn, and Zn and leaves the manganese mainly as an oxide.

Leaves in Solution: Al, As, B, Be, Cb, P, Ta, Ti, V, W, and Zr.

6. Separation with 8-hydroxyquinoline after treatment with  $H_2O_2$ :

Precipitates: Al, Be, Cu, Co, Fe, Mn, Ni, Sn, Sr, U, Zn, and Zr.

Leaves in Solution: As, B, Cb, Cr, Mo, P, Ta, Ti, W, and V.

Therefore, whether the final precipitation with 8-hydroxyquinoline in presence of  $H_2O_2$  is preceded by 4, 5, or both, and also by 2 or 3, depends upon the composition of the steel and the elements it is necessary to avoid.

**Weight of Sample.**—With the exception of aluminum steels, at least 5 g are always used. In aluminum steels the weight of sample is varied from 1 to 3 g according to the aluminum present.

**Solutions Required** are given at the end of this section.

**Blank.**—A blank test or a standard sample of steel should be analyzed in parallel with each analysis or set of analyses.

### Procedure

**Solution of Sample.**—Into a 500-ml Erlenmeyer flask, transfer 5 g of the steel, if the separation in step 2 is to be made with  $SO_2$ , or 10 g, if the separation is to be made with sodium bicarbonate. For the  $SO_2$  separation, time is saved by dissolving 7 g, diluting to 350 ml exactly, and filtering 250 ml through a dry paper without washing. Add 55 ml for 5 g, or 110 ml for 10 g, of dilute sulphuric acid (1:9). Heat to dissolve. Filter through a close 11-cm paper from the residue of alumina, silica, and carbon into a 600-ml beaker, or another 500-ml flask if a bicarbonate separation is to be made. Wash 2 or 3 times and dilute to 200 ml. If desired, determine alumina in the residue on the paper as described in the preceding section, otherwise discard it.

**I. A. Separation by Hydrolysis—With  $SO_2$  and Ammonia.**—To the filtrate, while stirring, add 60 ml of sulphurous acid (sp. gr. 1.02). Add methyl orange or methyl red, preferably the former. Add dilute ammonia (1:1) until a faint permanent precipitate is obtained, and the solution is yellow to the indicator. Stir and add more ammonia if necessary to keep the indicator yellow. Then add 10 ml of  $SO_2$  solution. Cover the beaker, boil the solution, and observe the precipitation, which should appear as a cloudiness in about 2 minutes. Continue boiling 5 or 10 minutes more until the color indicates that a little iron is precipitating. If cloudiness is not apparent, boil 15 minutes. Remove from the heat and filter immediately through a close paper. If the solution is not cloudy at this point, add a drop of ammonia, else precipitation of aluminum may be incomplete. Discard the filtrate and disregard any cloudiness, which is of no consequence. Wash the precipitate of alumina, which is contaminated with some iron and possibly other elements, a few times with water. With-

out delay, place the beaker in which precipitation was made under the funnel, punch a hole in the paper, and wash the precipitate through. Pour on the funnel 15 ml of hot dilute hydrochloric acid (1:1), which should dissolve all the precipitate. Use more acid if necessary, but as little as possible to keep down the quantity of sodium hydrate to be used later. Wash the paper 3 or 4 times with water, add 2 ml of nitric acid, and boil 2 minutes to oxidize the iron. If the next step involves a separation by electrolysis over a mercury cathode, oxidize the solution with ammonium.

**I. B. Alternate Separation with Sodium Bicarbonate.**—To the filtrate from the sulphuric acid solution, add 2 ml of a 20-per cent solution of sodium sulphite. While shaking, add from a burette an 8-per cent solution of sodium bicarbonate until a permanent precipitate is obtained, and then add 4 ml more. Note the total amount used for future reference and guidance, as chromium steels need a greater excess than carbon steels. Cover the flask, boil 1 minute, and let the precipitate settle. Filter immediately through an 18-cm filter paper of close texture and wash the paper and precipitate twice with hot water. If the filtrate becomes cloudy, ignore it, as it is due to oxidation of a little iron. Discard the filtrate. Treat the precipitate, which contains some iron and nickel and all the aluminum, chromium, vanadium, etc., as follows: Punch a hole in the paper and wash the precipitate back into the original flask. Pour over the paper exactly 15 ml of hot dilute hydrochloric acid (1:1) into the flask. Wash the paper once or twice with water. Heat the flask to dissolve the oxides. Add 4 to 5 ml of concentrated nitric acid or 7 to 10 ml of dilute  $\text{HNO}_3$  (sp. gr. 1.20), and boil 2 minutes, unless a separation by electrolysis over a mercury cathode is to be used.

**II. A. Separation with Sodium Hydroxide.**—This separation is made in essentially the same way whether a sulphur dioxide hydrolysis or a bicarbonate separation has been made. However, due to the greater quantity of iron that is precipitated with the bicarbonate separation, it may be necessary to take an aliquot part of the solution. Following a sulphur dioxide hydrolysis, all of the filtrate may be used except with high-chromium steels. In either case, the solution should contain approximately 3-per cent of sodium hydroxide to obtain a complete separation.

(a) *Procedure Following the Sulphur Dioxide-Ammonia Separation.*—To the solution containing the aluminum and some iron, add a 10-per cent solution of sodium hydroxide until a precipitate is obtained (about 50 ml) and then add, with constant stirring, 80 to 100 ml more of the sodium hydroxide. Dilute, if necessary, to 150 ml and boil 3 minutes. Let the precipitate settle and filter through an 11-cm filter paper, catching the filtrate in a 600-ml beaker which has been washed out with hydrochloric acid and water. Wash 3 times with hot water.



(b) *Procedure Following the Bicarbonate Separation.*—Add 40 ml of a 10-per cent solution of sodium hydroxide, which should nearly neutralize the solution; if a precipitate forms, dissolve it in hydrochloric acid. To a 600-ml beaker add 150 ml of the same sodium hydroxide solution. While stirring vigorously, add the neutralized solution in the 400-ml beaker to the caustic solution in the 600-ml beaker. If the iron has not been completely oxidized, causing the precipitate to appear dark in color, add 10 ml of hydrogen peroxide (3-per cent). Wash the beaker once and reserve it. Boil for 1 minute and cool the solution to room temperature, then transfer it to a 500-ml volumetric flask. Wash the beaker once and dilute the solution to the mark. Pour the solution back into the same 600-ml beaker, stir well, and let the precipitate settle. Decant about 300 ml of the clear solution into the 400-ml beaker used previously. Set an 11-cm filter paper in a funnel with water as usual. Start filtering the solution in the 400-ml beaker, but discard the first 25 to 30 ml. Then place under the funnel a 250-ml volumetric flask. Be sure that this flask has just previously been washed with hydrochloric acid and water, as any iron will cause error. Continue the filtration until the solution rises to the 250-ml mark. This position represents half of the original sample of 5 g or less.

**II. B. Separation by Electrolysis Over a Mercury Cathode.**—As a preliminary to the preparation of the solution for electrolysis, make sure that it is free of Cl and NO<sub>3</sub> ions, both of which are eliminated by fuming with H<sub>2</sub>SO<sub>4</sub>. Since only H<sub>2</sub>SO<sub>4</sub> is used in the preceding steps by this method, proceed with the preparation of the solution obtained as follows:

Boil down the acid solution from any of the separations above to a volume of approximately 75 ml, and neutralize with ammonia, using thymol blue, metacresol purple, or cresol red as an indicator if necessary. Then, add 0.2 ml of H<sub>2</sub>SO<sub>4</sub> and proceed with the electrolysis as directed for the determination of insoluble alumina.

### **Precipitation of Aluminum with 8-hydroxyquinoline**

Dilute the filtrate which contains the aluminum, uncontaminated with iron, to 250 ml if necessary. Add 2 drops of bromocresol purple indicator. Add 10 ml of 10-per cent solution of tartaric acid and follow with hydrochloric acid until the color of the solution is yellow. Add 5 ml of the latter acid in excess. Then carefully add ammonia until the color of the solution turns to purple, using dilute ammonia drop by drop when nearing the end point. It is imperative that this point is not overrun; if it should be, add dilute HCl until the color turns yellow and follow with dilute ammonia until it just turns purple again. Add 10 ml of 3-per cent hydrogen peroxide. Heat the solution to 50 to 55° C and add, with constant stirring, 10 ml of the 8-hydroxyquinoline solution, which causes a precipitate to form. If

the aluminum is high, continue the stirring, add 30 ml of an 18-per cent solution of ammonium acetate, and carefully add exactly 0.7 ml of ammonium hydroxide. Transfer the beaker to a stirring machine and stir 15 minutes. Remove and let stand, preferably in running water, until the solution is cool and the precipitate has settled. Filter the precipitate through an 11-cm No. 40 paper and wash at least 6 times with cold water, being careful to wash the top of the paper, because any of the 8-hydroxyquinoline will later be titrated as aluminum quinolate.

**Titration of Aluminum Quinolate.**—Transfer the paper to the original beaker to which have been added 40 ml of hydrochloric acid and 160 ml water. Heat (to 75° C) to decompose the aluminum quinolate. Cool to 20° C, dilute to 400 ml with water, and titrate as follows: Add from a burette 10 ml of standard bromate solution, this amount being sufficient for 0.04 per cent aluminum. To make sure enough of the bromate has been added, test the solution in the following manner: Stir for 1 minute, remove a drop on a stirring rod, add it to a drop of 10-per cent potassium iodide on a spot plate, then add a drop of starch, when the drop should turn blue, if enough bromate is present. If it does not turn blue, add more bromate, stir 1 minute, and test again. Continue thus until the test drop turns blue. Add to the solution 10 ml of 10-per cent potassium iodide. Stir to mix and titrate with thiosulphate solution until the yellow color begins to fade. Then add 2 ml of starch solution and continue the titration until the blue color disappears.

To another beaker, containing 40 ml hydrochloric acid and 360 ml water, add 10 ml bromate solution. Add 10 ml potassium iodide solution and titrate with thiosulphate as before. The solutions should be equal. If not, divide the ml of bromate by the ml of thiosulphate to find the value of thiosulphate. For example, if 10 ml bromate require 10.5 ml of thiosulphate, the value of 1 ml of the thiosulphate is  $10.0 \div 10.5 = 0.952$ .

**Calculation.**—1 liter of *N* solution of bromate equals 1/12 of 26.97 g Al or 1 ml equals 0.0022475 g Al. If desired, a solution for magnesia, which is 0.0992 *N*, may be used, when 1 ml of the bromate equals 0.000223 g Al and 0.00446 per cent aluminum on a 5-g sample. Then multiply the number of ml of thiosulphate by the factor found above and deduct from the bromate used. Multiply this difference by 0.00446 to obtain per cent Al.

**Example:**

	0.0992 <i>N</i>	0.1112 <i>N</i>
Bromate =	10.0	10.0
Thiosulphate	3.8	4.4
Bromate = Al	<u>6.2</u>	<u>5.6</u>
	0.00446	0.005
	<u>0.027642</u>	<u>0.028</u>

Al = 0.028

**Blank.**—A blank should be run on the same amount of sodium hydroxide. Take 100 ml (or as required) of the solution. Dilute to 250 ml. Add tartaric acid and neutralize and precipitate any aluminum as in the test. Filter, titrate, and deduct. It is found that the blank is very low—of the order of 0.002 per cent on a 5-g sample basis.

Also, a uniform standard sample of steel on which the aluminum has been accurately determined may be used to determine the blank, this sample being run through all steps of the analysis in parallel with the analysis of the unknown sample.

### **Procedures for Aluminum and Alumina in High-Chromium Steels, Including Stainless and Heat-Resistant Steels**

For the determination of aluminum by the preceding method, chromium must be separated. When total aluminum is desired, the chromium is most conveniently eliminated by volatilizing it as directed under *Chemical Separations*. This method, however, has not been investigated to determine if the combined aluminum will remain insoluble under the conditions of the volatilization, but the following method has given satisfactory results for both Al and  $\text{Al}_2\text{O}_3$ .

#### **Lead Chromate Separation Followed by Titration of Aluminum as the Quinolate**

**Solution of the Sample and Separation of  $\text{Al}_2\text{O}_3$ .**—Transfer 7 g of the sample to an 800-ml beaker. Add 120 ml of water and 80 ml of perchloric acid (55-per cent) and heat gently until the cuttings have dissolved. Filter through an 11-cm close paper and wash with hot water and dilute HCl (2-per cent). Reserve the residue for the determination of  $\text{Al}_2\text{O}_3$  as directed later, and treat the filtrate as follows:

**Oxidation and Separation of Chromium.**—Evaporate the filtrate rapidly until it begins to fume, then cover the beaker and continue the heating for 10 minutes after perchloric acid is condensing on the inner wall of the beaker. Grasp the beaker with tongs, remove it from the heat, swirl the contents, and cool rapidly by dipping in and out of water. Add 80 ml of cold water, stir the solution with a stirring rod, and boil it for 3 minutes. Remove the beaker from the heat, and immediately add, while stirring vigorously, 1 ml (20 drops) of 0.5 molar silver perchlorate solution and a volume of 0.5 molar lead perchlorate sufficient to precipitate the chromic acid and leave the concentration of the solution 0.02 molar with respect to the excess of lead perchlorate. To obtain a correct excess, add 4 ml of the lead perchlorate solution for each 100 mg of chromium present and 4 ml additional for each 100 ml of solution. Cool the beaker and contents in running water, stirring occasionally, and filter the solution through a large paper into an 800-ml beaker. Wash the filter and precipitate 3 or 4 times with cold water and discard the precipitate.

**Removal of Excess Lead and Sulphide.**—To remove the lead, add to the cold solution 10 ml of ammonium polysulphide, and 15 ml of HCl. While stirring, add slowly 20 ml more of the ammonium polysulphide, and continue to stir the solution for 1 or 2 minutes to make sure all the iron is reduced. If in doubt, remove a drop of the solution and add it to a drop of a sodium thiocyanate solution (the thiocyanate test for ferric iron). Cool, if necessary, and filter through an 18.5 cm filter paper. Rinse the beaker and wash the filter and contents lightly with cold water. Discard the precipitate and boil the filtrate 20 minutes to expel  $\text{H}_2\text{S}$ .

### Determination of Aluminum

Cool the solution somewhat, add 60 ml of sulphurous acid, and continue for the separation of aluminum as directed above for aluminum in plain-carbon steel.

### Determination of Alumina

Transfer the paper containing the acid-insoluble residue to a 100-ml beaker, add 10 ml of perchloric acid (70- to 72-per cent), and heat cautiously to destroy the paper, gradually increasing the temperature until the acid is fuming. Cool the beaker and contents, and add 48 ml of cold water. Filter the solution through a small close paper and wash with dilute hydrochloric acid (2-per cent). If the steel contains molybdenum, wash with the dilute acid, next with water, then with dilute ammonia (1 + 10) and water, and finally with dilute acid. Transfer the paper and contents to a weighed platinum crucible, ignite, and treat with a drop of  $\text{H}_2\text{SO}_4$  (1:1) and HF to volatilize the silica. Evaporate to dryness, ignite, and weight as  $\text{Al}_2\text{O}_3 + \text{TiO}_2$ . If the steel contains titanium, fuse the residue with acid sodium sulphate or potassium pyrosulphate, and determine Ti by color. Calculate Ti to  $\text{TiO}_2$  and subtract to find the weight of  $\text{Al}_2\text{O}_3$ .

### Solutions Required

**Sodium Hydroxide.**—Use C.P. or reagent grade, preferably in pebble form. Each test will require about 10 g. The solution should be made as used. Before running a number of tests, dissolve the requisite number of grams in 13 to 15 times as much water. It dissolves easily and need not be filtered.

**Sulphuric Acid.**—Transfer 500 ml of dilute sulphuric acid (1:1) to a  $\frac{1}{2}$ -gallon bottle and add 2000 ml of water.

**Sulphurous Acid or  $\text{SO}_2$ -Water.**—Cylinder gas is preferable, though it may be generated by treating a sulphite with dilute sulphuric acid. Pass the  $\text{SO}_2$  gas through a long tube extending to the bottom of a 1000-ml cylinder which contains about 1000 ml of cold water. Allow a hydrometer (1.00-1.20) to float in the water and pass the gas until

the hydrometer rises to a specific gravity of 1.02. Shut off the gas and transfer the solution to a liter bottle, preferably rubber-stoppered.

**Sodium Bicarbonate Solution.**—Dissolve 80 g of C.P. sodium bicarbonate in water and dilute to 1000 ml.

**8-Hydroxyquinoline.**—Dissolve 25 grams of the compound in 50 ml of acetic acid and pour into 950 ml of water at 60° C. Cool and filter. The amount required is 3.5 ml for each 0.1 per cent on a 5-g sample (or .005 g), plus an excess of 5 ml. Ten ml are sufficient for 0.12 per cent aluminum.

**Indicator Solution: Bromcresol purple.**—Weigh 100 mg and transfer to a small beaker. Add 3.5 ml of 0.16 *N* sodium hydroxide. Stir until dissolved and dilute to 100 ml.

**Bromate Solution.**—Dissolve 2.8 g potassium bromate and 10 g potassium bromide in water and dilute to 1000 ml. This solution is stronger than required and must be standardized and diluted.

**Sodium Thiosulphate Solution.**—Dissolve 24.8 g of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1000 ml water.

These solutions are made 0.099206 *N* so that 1 ml = 0.1 per cent magnesia on a 0.5-g sample. The solution can also be made 0.1112 *N*, when 1 ml = 0.005 per cent Al. The standardization may be done in either of two ways, the first being preferred by many.

(1) For a normality of 0.099206, weigh 0.1963 g of arsenious oxide ( $\text{As}_2\text{O}_3$ ) of the Bureau of Standards, and transfer to a 600-ml beaker. Add 10 ml water and 5 ml of the 10-per cent sodium hydroxide solution. Stir to dissolve. Add 75 ml strong hydrochloric acid and 325 ml water. The gravity of the acid should be 1.03. Add a few drops of methyl orange indicator and then titrate with the bromate solution slowly while stirring until the solution turns colorless, about 40 ml being required. Add the last few drops very slowly before the end point. Adjust the solution so that exactly 40 ml are required. Standardize the thiosulphate solution against the bromate as described above.

(2) For the second method of standardization proceed as follows: Standardize the thiosulphate against potassium permanganate (0.1 *N*) which has been standardized against sodium oxalate. Then standardize the bromate against the thiosulphate.

### Determination of Total Aluminum in High-Silicon Steels

The following procedure was developed for total aluminum in high-silicon steels, particularly those grades used for electrical sheets. The method is designed to give accurate results representing the total aluminum in the absence of Ti, V, Cb, Ta, and Zn. By fusing and treating the final ignited precipitate, contamination by Ti and V is detected and the final result corrected if but one of these elements is found.

The other elements, Cb, Ta, and Zn, are not likely to occur in this steel.

### **Solution of the Sample**

Transfer 2 g of the sample to a 250-ml platinum dish and add 30 ml of dilute HCl (2:1) and 10 to 15 ml of HF (48-per cent). Apply heat gently till the cuttings are dissolved, and evaporate rapidly until salts begin to separate, then cautiously to avoid spitting until the residue is approaching dryness. Add 10 ml of  $\text{H}_2\text{SO}_4$ , distributing the acid about the upper edge of the ring of salts in the dish. Continue heating the dish carefully, keeping the acid spread over the salts until the acid is fuming strongly. Cool somewhat and add 75 ml of water to dissolve the sulphates.

### **Initial Separation with Phosphate**

Transfer the solution to an 800-ml beaker, dilute to 250 ml, and add 20 ml of a 10-per cent solution of ammonium phosphate. Add ammonia while stirring until a faint precipitate appears. Then add 1.5 ml of HCl or 3 ml of dilute HCl (1:1) and 60 ml of a 20-per cent solution of sodium thiosulphate. Heat to boiling and add successively 8 ml of glacial acetic acid and 20 ml of a 20-per cent solution of ammonium acetate. Boil for 10 minutes, allow the precipitate to settle for 20 minutes, add some paper pulp, and filter. Wash the filter once or twice with water and dissolve the precipitate with hot dilute HCl (1:1), collecting the solution in a 200-ml beaker, and wash the filter thoroughly with water.

### **Separation by Electrolysis Over a Mercury Cathode**

Add 1 ml of  $\text{H}_2\text{SO}_4$  (1:1) to the solution and evaporate rapidly to 15 to 20 ml and dilute to 75 ml with cold water. Neutralize the solution with dilute ammonia (1:1) and add 0.2 ml of  $\text{H}_2\text{SO}_4$ . Transfer the solution to a Melaven cell for electrolysis over mercury and electrolyze the solution for 30 minutes, stirring the solution constantly and applying a current of 5 amps for a mercury surface diameter of 7.5 cm. Cut the current back to about 0.5 amp and withdraw the solution into a 100-ml beaker. Rinse the cell with a little water and filter the solution into a 600-ml beaker and wash the paper with cold dilute  $\text{H}_2\text{SO}_4$  (1-per cent).

### **Precipitation and Determination of Aluminum as Phosphate**

Add 2 drops of methyl orange indicator solution to the solution and stir in 10 ml of a 10-per cent solution of ammonium phosphate. Add dilute ammonia (1:4), dropwise, with constant stirring until the color changes. Add 1 ml of dilute HCl (1:9) and 25 ml of a 20-per cent solution of ammonium acetate. Boil the mixture 2 minutes and let the precipitate settle for about 20 minutes. Add paper pulp, filter,

and wash thoroughly with warm 2-per cent solution of ammonium nitrate. Transfer the paper and contents to a weighed platinum crucible, dry, ignite gradually until the paper is consumed, and increase the ignition temperature to  $1000^{\circ}\text{C}$  ( $1832^{\circ}\text{F}$ ) until the weight is constant. Cool and weigh as  $\text{AlPO}_4$ . Multiply the weight of  $\text{AlPO}_4$  by 100 times 0.2211 and divide by 2 to find the per cent total Al in the sample.

To test for V and Ti, fuse the ignited precipitate with a little acid sodium sulphate, dissolve the melt in water, acidify with  $\text{H}_2\text{SO}_4$ , add  $\text{H}_2\text{O}_2$ , and estimate Ti + V by color. If a color develops, test for V by adding NaF, which will cause the titanium color to fade.

# Determination of Arsenic

## Occurrence of Arsenic in Steel

Unless materials are carefully selected, arsenic may occur in any steel, particularly that made by the open-hearth, electric, and other scrap consuming processes. Except for some special purposes, small percentages of arsenic have little effect upon the properties of the steel, and to produce some special grades, it has been added to steel, more so in foreign than in American-made steels.

## Methods Available

Only two noteworthy methods are available for separating arsenic from the iron and other elements with which it may be combined in steel, and both of these depend upon the volatility of  $\text{AsCl}_3$ . To avoid loss, the arsenic must be oxidized to arsenic acid as the sample is dissolved, then reduced to arsenious acid, converted to  $\text{AsCl}_3$ , and distilled. After absorption of the  $\text{AsCl}_3$  in water, the arsenic may be determined by titration with  $\text{KCNS}$ , iodine, or potassium bromate, or by precipitation with  $\text{H}_2\text{S}$  and weighing as  $\text{As}_2\text{S}_3$ .

In carrying out determinations, the analyst must guard against two sources of error. The first refers to the danger of contamination from tin and antimony. Stannic chloride boils at  $114^\circ \text{C}$ , arsenic trichloride at  $130^\circ \text{C}$ , and antimony trichloride at  $220.2^\circ \text{C}$ . Distillation of any but a trace of antimony trichloride is prevented by keeping the distillation temperature below  $112^\circ \text{C}$ , and the distillation of tin is prevented by phosphoric acid, which should be added, if very little phosphorus is present. The tin phosphate formed can be broken up by the addition of a mixture of hydrochloric (3 parts) and hydrobromic (1 part) acids, and the  $\text{SnCl}_4$  distilled after arsenic has been separated.

The second source of error lies in the use of rubber stoppers or tubing, which may absorb  $\text{AsCl}_3$  vapor in varying amounts. Also, if the same rubber is used repeatedly, it may absorb  $\text{AsCl}_3$  in one determination and give up part of the arsenic in another. Therefore, glass-stoppered flasks and glass-to-glass connections are recommended for use in all determinations of arsenic.

For umpire and other analyses requiring exactness, especially if the proportion of arsenic to be determined is small, an all-glass apparatus such as that devised by Sherrer<sup>1</sup> is recommended.

## Blanks

To guard against arsenic from glassware or other sources, a blank test should be carried through all steps with each set of analyses.



## Methods for Solution of the Sample and Separation of Arsenic

### Procedure Dissolving the Sample in Nitric Acid Followed by Reduction and Distillation of $\text{AsCl}_3$

**Solution of the Sample.**—Transfer 10 g of drillings to a suitable distillation flask, preferably glass-stoppered with side outlet, and dissolve in 150 ml of nitric acid (1.2 sp. gr.). Add 50 ml of sulphuric acid and evaporate until copious fumes of sulphuric acid are given off. Cool the flask, add 50 ml of water, and evaporate again until copious fumes of sulphuric acid are evolved. Cool, add 50 ml of water, and cool again.

**Separation of Arsenic.**—Add to the mass in the flask, 20 g of ferrous ammonium sulphate to reduce the arsenic acid and 3 to 5 ml of ortho-phosphoric acid (85-per cent) if required to hold back tin. Pour in 150 ml of concentrated hydrochloric acid to convert the arsenious acid to the volatile arsenic trichloride. Close the flask with a stopper carrying a tube bent twice at right angles, if the flask used does not have a side outlet, and connect glass-to-glass with a rubber tube to a 50-ml pipette, the point of which dips about  $\frac{1}{4}$  inch (6 mm) into 300 ml of water in a beaker which is preferably partly immersed in ice water contained in another beaker. Heat the liquid in the flask gradually until it boils, during which period the bulb of the pipette becomes hot, then cool, and continue the distillation until the bulb of the pipette becomes heated again. If the arsenic is above 0.10 per cent, remove the flask from the heat, loosen the stopper at once, add more of the ferrous sulphate and hydrochloric acid, and repeat the distillation. For exact work, repeat the distillation in every analysis. Determine the arsenic by one of the methods given below.

### Procedure Dissolving in a Mixture of Hydrochloric Acid and Potassium Chlorate

**Solution of the Sample.**—Transfer 10 g of the coarser cuttings of the sample, or less if arsenic is above 0.010%, to the distillation flask, add 10 g of potassium chlorate, connect the flask to the absorption apparatus as directed in the preceding method, and place the bottom of the flask in cold water, ice water if available. Cool 100 ml of concentrated hydrochloric acid, add 5 ml of a saturated water solution of potassium chlorate, and, after adding 10 to 15 ml of  $\text{HNO}_3$  to the absorption beaker, transfer the mixture to the distillation flask. Alternately, add 20 ml of water to the flask and arrange to add the acid slowly to control the speed of reaction of the acid on the sample. If all the acid has been added, control the speed of reaction of the acid with the cuttings, keeping it going continuously at a moderate rate, by raising or lowering the temperature. If the action is or becomes slow, add 2 or 3 g of additional  $\text{KClO}_3$  and apply heat from a steam or sand bath till solution is complete, finally heating to the expulsion of  $\text{HCl}$

and free chlorine. Cool the flask and boil off the HCl and chlorine from the nitric acid used as a trap. Add the latter with a little phosphoric acid—if needed to hold back tin—to the distillation flask, and rinse the pipette thoroughly with water. Add 300 ml of cold water to the beaker, 100 ml of HCl, and 30 g of ferrous sulphate or cuprous chloride,  $\text{Cu}_2\text{Cl}_2$ , to the flask, and distill the  $\text{AsCl}_3$  as directed above.

### Methods for Determination of Arsenic

Following the separation of the arsenic it is determined gravimetrically by precipitating with  $\text{H}_2\text{S}$  or volumetrically by titration with potassium bromate, both as directed below. The reactions involved in each method are simple and may be represented thus:

Gravimetric method:  $2\text{AsCl}_3 + 3\text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3 + 6\text{HCl}$ .

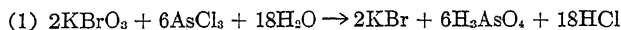
Volumetric method:  $2\text{KBrO}_3 + 6\text{AsCl}_3 + 18\text{H}_2\text{O} \rightarrow 2\text{KBr} + 6\text{H}_3\text{AsO}_4 + 18\text{HCl}$ .

### Gravimetric Method Weighing as $\text{As}_2\text{S}_3$

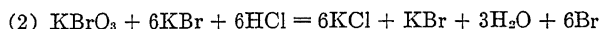
Heat the solution in the beaker which contains the distilled  $\text{AsCl}_3$  to about  $70^\circ \text{C}$ , and pass a rapid current of hydrogen sulphide through it until it is completely saturated. Remove the excess of hydrogen sulphide by a current of carbonic acid ( $\text{CO}_2$ ), and when the solution smells very faintly of hydrogen sulphide, filter off the yellow precipitate of arsenious sulphide on a Gooch crucible or on a counterpoised filter, wash with water, then with alcohol, then with pure carbon disulphide, dry at  $100^\circ \text{C}$ , and weigh as arsenious sulphide, which contains 60.89 per cent arsenic. Correct for any blank found and calculate the per cent arsenic in the sample.

### Volumetric Method Titrating with Potassium Bromate

**Principles of the Method.**—In this method the  $\text{AsCl}_3$  in an adjusted HCl solution is titrated with  $\text{KBrO}_3$  using methyl orange as an indicator, which is brominated to a colorless compound when the reaction between the  $\text{KBrO}_3$  and  $\text{AsCl}_3$  has been completed. As already noted, this reaction is:



Bromination of the methyl orange involves the following reaction:



With arsenic present the KBr required by reaction (2) is supplied in advance by reaction (1), but with little or no arsenic present insufficient KBr is present to complete the bromination of the methyl orange. This drawback, however, is readily overcome by adding KBr to the  $\text{KBrO}_3$  solution, as noted below. Regarding the relative amount of HCl required in the titrating solution, there have been slight discrepancies. This point was accordingly investigated by Duquesne

Laboratory, where it was found that results are highly unsatisfactory if the solution to be titrated contains less than 5 per cent or more than 25 per cent HCl, but satisfactory with 10 to 20 per cent. On a gravity basis, a specific gravity of 1.02 corresponds to 11 per cent HCl and 1.03 to 18 per cent.

**Special Solution Required.**—*Standard 0.05 N Potassium Bromate.* Dissolve 1.392 g of pure, dry  $\text{KBrO}_3$  and 5 g of KBr in water and dilute to 1 liter. One ml is equivalent to 0.001874 g of arsenic.

**Procedure.**—Neutralize the cold solution of  $\text{AsCl}_3$  by adding NaOH in small pellets until alkaline, and then adjusting with fairly dilute solutions of NaOH and HCl. Acidify with HCl to 10 per cent by volume (10 ml of concentrated HCl per 100 ml of solution). Alternately, suspend a small hydrometer in the solution and dilute until the specific gravity is between 1.02 and 1.03. Add 5 drops of methyl orange, stir, and then add from a burette a standard solution (0.05 N) of  $\text{KBrO}_3$  until the pink color just disappears, being careful not to overrun the end point, which occurs through reaction of free bromine on the methyl orange, resulting in the complete destruction of the indicator.

Titrate the blank in the same way, multiply the corrected volume of the bromate solution used by its arsenic titer, and divide by the weight of sample used to find the per cent arsenic.

If the purity of the reagent is in doubt, recrystallize from water and dry at  $180^\circ \text{C}$ , or standardize against National Bureau of Standards Standard Sample No. 83 arsenic trioxide, as described under *Determination of Aluminum*.

#### Text References

1. Sherrer, J. A., Research Paper 253, *J. Research Nat'l Bur. Standards*, 16, No. 3, March, 1936.
2. Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel," New York, John Wiley and Sons, Inc., 1931.

# Determination of Tin

## Occurrence of Tin

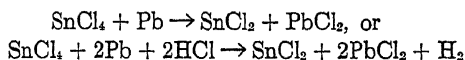
Tin has become widely distributed in iron and steel and is likely to be found in any steel made without special attention to raw materials used, particularly the scrap. Up to 0.10 per cent tin has no noticeable effect upon the physical properties of structural steels, though 0.05 per cent is the limit for tool steels; and it may favorably affect many other properties. However, in larger proportions its effects are generally injurious. In these small percentages, tin may interfere in the determination of small percentages of several other elements. Its presence, therefore, is not of so much interest metallurgically as chemically, and as a rule, the analyst is dealing with small proportions, 0.001 to 0.05 per cent, except in work on tin plate or special heats.

## Methods Available

In all methods tin is determined by titration of the tin as stannous chloride with iodine or potassium iodate solution, according to the reaction.



Preliminary to titrating, the stannic chloride is reduced with pure nickel, antimony, or test lead, thus:



Arsenious chloride, or oxide, of course, is titrated with iodine or iodate. Chromium, molybdenum, and vanadium chlorides are also reduced and partly or completely oxidized by iodine; and tungsten interferes by reduction to a colored compound which obscures the end point, making it necessary to separate the tin from these 4 elements, at least the first 2 of which are also found widely distributed in steels in small but varying percentages. Troublesome peculiarities are encountered from the beginning of an analysis. For example, solution in  $\text{H}_2\text{SO}_4$  leaves about  $\frac{1}{4}$  of the tin in the residue, while any evaporation of hydrochloric acid solutions results in loss of some of the tin through volatilization of the chloride. These are some of the reasons why methods based upon direct titration of tin in the original hydrochloric acid solutions are unreliable, and suitable only for routine or control work. The first two methods that follow are based upon the work of J. A. Sherrer of the National Bureau of Standards. See Research Papers No. 415 and No. 871, the second being quoted from R. P. No.

415, with the exception of the explanation as to the size of sample, the modification permitting the use of pure shot nickel for reducing the  $\text{SnCl}_4$ , and for steels not decomposed with  $\text{HNO}_3$ .

### METHODS OF DETERMINATION

#### Special Solution Required

**Standard Iodine or Potassium Iodate.**—Either iodine or potassium iodate may be used, though most analysts prefer the iodate. For tin under 0.05 per cent a 0.01 *N* solution is suitable, and 0.05 or 0.1 *N* solution for tin in larger proportions. One ml of 0.1 *N* solution is equivalent to 0.006 g of tin. In steel laboratories the solutions used for titrating sulphur may be utilized. The solutions are generally prepared so that 1 ml = 0.01 per cent sulphur, and for 5-g samples the normality = 0.03119 = 0.037 per cent tin. For 1 ml to equal 0.01 per cent tin on a 5-g sample, the normality must be 0.00842. The solutions are prepared in the usual manner and standardized against pure tin.

#### Distillation: Volumetric Method

##### Application of the Method

This method has been devised for application to any steel and for any percentage of tin, by varying the weight of sample used.

##### Weight of Sample

For tin under 0.10 per cent, which will include nearly all carbon and alloy steels, use a sample of 10 g. Decrease this weight to 5 g for detinned scrap, and to 1 g for materials containing approximately 1.00 per cent tin.

##### Procedure

**Solution of Sample and Separation of Tin.**—Proceed as described for the determination of arsenic in the preceding section, using the  $\text{HCl-KClO}_3$  method for steels insoluble in nitric acid. In the presence of arsenic, add phosphoric acid as directed in the method, and distill off the  $\text{AsCl}_3$  as for a determination of arsenic and then distill the tin. In the positive absence of arsenic omit the phosphoric acid. Add to the hydrochloric acid enough hydrobromic acid to decompose the tin phosphate, very little being sufficient if no phosphoric acid has been added, and distill in the manner directed for arsenic. In very exact work repeat the distillation, but titrate each portion separately.

**Reduction of  $\text{SnCl}_4$  and Titration of  $\text{SnCl}_2$ .**—Transfer the distillate, representing a hydrochloric or hydrochloric-hydrobromic acid solution of  $\text{SnCl}_4$ , to a 500-ml flask, and dilute with water to give a solution containing 25 to 30 per cent by volume of these acids. Equip the flask with a bunsen valve and displace all the air with  $\text{CO}_2$ . Add test lead,

pure antimony, or pure shot nickel in excess, continue to pass  $\text{CO}_2$ , and boil till all the  $\text{SnCl}_4$  is reduced, about 30 minutes with test lead. Continue to pass  $\text{CO}_2$  and cool the solution to  $10^\circ \text{C}$ . Then without shutting off the stream of  $\text{CO}_2$ , raise the stopper to one side to admit the tip of a burette, add 5 ml of freshly prepared starch solution, and titrate with the standard iodine or potassium iodate solution to the first appearance of a blue color. Multiply the ml of standard solution used by its tin titer and by 100 and divide by the weight of sample taken, if the solution is not made up so that each ml is equivalent to a certain percentage for the weight of sample taken.

### Umpire Method

#### Weight of Sample

The weight of sample and acid used for dissolving it are varied according to the tin present as follows:

Per Cent Tin	Weight of Sample	Ml of $\text{HNO}_3$ (1:4)	Ml of $\text{H}_2\text{SO}_4$ (1:5)
0.001 to 0.01	25 g	600	300
0.01 to 0.05	10 g	250	130
0.05 to 0.20	5 g	140	75

### I. Solution of the Sample

**1. Procedure for Irons, Plain-Carbon Steels, and Alloy Steels Decomposable by Nitric Acid.**—Treat the sample of iron or steel in a 600-ml beaker with the prescribed volume of dilute nitric acid (1:4), cover with a watch glass, and warm gently until vigorous action ceases. Bring nearly to the boiling point, continue heating until the sample is completely decomposed, and then boil for about 5 minutes. Gradually add a saturated solution of potassium permanganate until it is present in slight excess (usually 3 to 5 ml is required), and boil for about 5 minutes. Brown oxides of manganese separate if sufficient permanganate has been added. Cautiously add sulphurous acid until the oxides disappear, and boil for 5 to 10 minutes to expel sulphur dioxide.

(a) *Treatment When Tungsten is Absent.*—If any undecomposed matter remains, filter, wash, and reserve the filtrate. Occasionally, the steel leaves a residue which is so finely divided that it passes through the filter. Treat such steels as in (b). Transfer the filter paper and residue to a 500-ml Erlenmeyer flask, and add 10 to 12 ml of sulphuric acid (specific gravity 1.84) and about 25 ml of nitric acid (sp. gr. 1.42). Heat gently until the first vigorous action is over, then raise the temperature so that the nitric acid is expelled in 30 to 45 minutes and the sulphuric acid is fuming gently. Continue the addition and evaporation of nitric acid in small amounts until the sulphuric acid does not show any evidence of organic matter on fuming. The sulphuric acid should not be too strongly heated, as insoluble chromium sulphate may be formed. Two or three treatments with nitric acid

usually suffice. Dilute to about 100 ml with distilled water, add about 10 g of tartaric acid, and boil until all soluble matter is in solution, and filter if necessary. Neutralize with ammonium hydroxide and add to the reserved filtrate, then treat as in II for the precipitation with  $H_2S$ .

(b) *Treatment When Tungsten is Present.*—Allow the solution to stand overnight, carefully decant the clear liquid, and set it aside. Treat the carbide residue, which always contains a little tin, and the small amount of liquid remaining in the beaker with about 20 ml of sulphuric acid and 30 ml of water. Heat just below the boiling point until no more bubbles of gas are given off and then evaporate until the sulphuric acid fumes gently. Add 10 to 15 ml of nitric acid (sp. gr. 1.42) and again evaporate to slight fumes of sulphuric acid. Repeat till all black residue is decomposed. Dilute to about 100 ml with distilled water, add a small excess of ammonium hydroxide and about 10 g of tartaric acid. When the tartaric acid is in solution again, add a slight excess of ammonium hydroxide. If the solution is not clear, add more tartaric acid. Make slightly acid and filter off any insoluble matter which may be present. Neutralize and add to the reserved solution, and treat as directed in II for the precipitation with  $H_2S$ .

## 2. Procedure for Alloy Steels not Decomposable by Nitric Acid—

(a) *Treatment in the Absence of Tungsten or Other Insoluble Matter.*—Treat 10 g of the sample with 130 ml of sulphuric acid (1:5). Heat on the steam bath until vigorous action ceases. Place on a hot plate, heat gently until decomposition is complete, and then boil for about 5 minutes. Gradually add an excess of crystals of potassium permanganate (5 to 7 g is usually required) or oxidize with 25 ml of nitric acid (1:1) and then add an excess of a saturated solution of permanganate. Boil for about 5 minutes. Oxides of manganese should persist. Add 25 to 50 ml of a saturated solution of sulphurous acid and boil for about 5 to 10 minutes to remove sulphur dioxide. The solution is now ready for treatment with hydrogen sulphide as in II below.

(b) *Treatment in the Presence of Tungsten or Other Insoluble Matter.*—Dissolve 10 g of sample in sulphuric acid, filter, treat the filtrate as in (a) above, and reserve it. Decompose the paper and residue with nitric and sulphuric acids as in 1 (b) to recover tin, which is always present. When tungsten is present, observe that a darkening of the residue takes place on fuming with sulphuric acid, and do not mistake it for organic matter; moreover, fume the sulphuric acid very gently when chromium is present, for strong fuming may yield insoluble compounds of chromium. Dilute to 100 ml with distilled water, heat to boiling, and digest for  $\frac{1}{2}$  to 1 hour. Add a small excess of ammonium hydroxide and 10 to 15 g of tartaric acid. When the tartaric acid has dissolved again, add a small excess of ammonium hydroxide, and

digest on the steam bath until solution is complete or nearly so (usually  $\frac{1}{2}$  to 1 hour). Then add an excess of about 5 ml of sulphuric acid (sp. gr. 1.84) and digest on the steam bath for  $\frac{1}{2}$  hour, by which time solution is generally complete. If not, filter, decompose the filter and residue as before, and unite the solution with the other. Neutralize with ammonium hydroxide, add to the reserved filtrate, and treat the combined solutions as in II below.

## II. Precipitation and Separation of Tin with $H_2S$ and Ammonia

Cool to room temperature, dilute to about 500 ml for a 5-g sample or to 800 ml for 25 g, and treat with a rapid stream of hydrogen sulphide for 30 to 45 minutes. Let settle for 1 to 2 hours, filter, and wash with a slightly acid 5-per cent solution of ammonium sulphate which has been saturated with hydrogen sulphide.

Transfer the paper and precipitate to a 500-ml Erlenmeyer flask and decompose with sulphuric and nitric acids as in 1 (a). Fume strongly. Cool and dilute to 100 ml with distilled water.

If the sample contains tungsten, add about 10 g of tartaric acid. When the acid has dissolved, add a slight excess of ammonium hydroxide and heat to boiling. The solution should be clear. Add an excess of about 10 ml of sulphuric acid (sp. gr. 1.84), filter, and wash. Dilute the filtrate to about 550 ml. Again treat with hydrogen sulphide, filter, wash, dissolve paper, and precipitate and dilute to 100 ml as before.

Boil until the solution is clear or all soluble matter is in solution. Add 15 ml of hydrochloric acid, and filter to remove sulphur, also graphite in the case of cast irons, and wash with water. Discard the filter, as it contains but a trace of, if any, tin.

Add about 40 mg of iron as chloride or sulphate to the filtrate, which should have a volume of about 200 ml, heat to boiling, and add dilute ammonium hydroxide (1:1) until in moderate excess (5 to 10 ml) and boil. Filter and wash 3 or 4 times with dilute ammonium hydroxide (2:100), and 2 or 3 times with water. Do not permit the filter to run dry, for this causes filtration to become very slow in some cases. Discard the filtrate or use it to estimate copper and molybdenum by color and dissolve the precipitate by passing a hot mixture of 80 ml of hydrochloric acid and 100 ml of distilled water through the paper, catching the solution in a 500-ml Erlenmeyer flask.

## III. Reduction and Titration of Tin

Dilute to about 350 ml, add a solution of about 10 to 15 mg of antimony as chloride or sulphate, and then about 10 g of test lead or enough shot nickel to give an excess. Connect with an air condenser (Fig. 15) and start a stream of carbon dioxide through the apparatus. Heat to boiling and boil gently for 30 to 40 minutes. Cool in a bath of ice water and regulate the current of carbon dioxide so as to prevent



## ANALYSIS OF STEELS

back pressure. This may be detected by placing the bubble tube on the end of the air condenser. When the solution has cooled to at least  $10^{\circ}\text{C}$ , add through the air condenser 5 ml of clear starch solution, preferably containing about 30 g of KI per liter to reduce the starch blank. Remove the plug in the third hole of the stopper and immediately insert the tip of the burette (10 ml capacity in the usual case) containing the standard iodine, or iodate solution. Titrate to the first permanent shade of blue. Deduct the volume required for a blank run, and multiply by the tin titer of the solution.

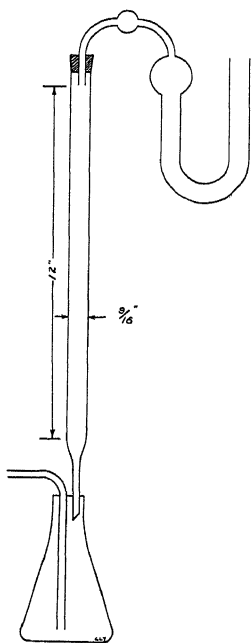


FIGURE 15. Apparatus for reduction of tin.

For material containing less than 0.05 per cent of tin, use a 0.01 *N* solution; for higher percentages, use 0.1 *N* solution. The theoretical titer may be used in the ordinary case. One ml of 0.01 *N* iodine equals 0.0006 g of tin (0.0005935 theoretical). If more than 1 per cent of tin is in question, or exceptional accuracy is required, the titer should be obtained by standardizing against pure tin.

### Rapid Control Method for Tin

#### Solution of Sample in HCl Followed by Direct Titration of Tin

This method is applicable only to carbon steels containing little copper and no chromium, molybdenum, or vanadium.

**Special Solutions Required.**—Standard Solution of potassium iodate, preferably 0.00842 *N* so that 1 ml equals 0.01 per cent tin on 1 g of sample. Usually, the solution used for titrating sulphur by the evolution method is employed, 1 ml of which equals 0.01 per cent sulphur or 0.0074 per cent tin on a 5-g sample.

**Apparatus.**—Since solution of the steel in HCl is depended upon to reduce the tin, the apparatus is set up to exclude air following solution to avoid possibility of oxidizing any of the stannous chloride formed. For this purpose, an evolution sulphur flask is equipped with a 2-hole rubber stopper bearing a funnel tube with stopcock and a delivery tube bent at right angles. The exit end of the delivery tube is in turn connected to a 3-way stopcock with short arms. One of the free arms of the stopcock is connected to the stem of a 50-ml pipette which has been bent at a right angle. The other stem of the pipette is inserted into a 10-inch by 1-inch test tube containing the ordinary solution used for absorbing  $\text{H}_2\text{S}$  in evolution sulphur determinations. Finally, the third arm of the stopcock is connected to a piece of glass tubing bent at a right angle, the long arm of which dips into a second 10-inch by 1-inch test tube containing 10 ml of dilute hydrochloric acid. Just before a determination is begun 50 ml of a 6-per cent solution of sodium bicarbonate is added to the acid, which reacts to form a little  $\text{CO}_2$  to drive out the dissolved oxygen from the excess bicarbonate solution, and this solution is drawn up to fill the tube as far as the stopcock.

**Procedure.**—With the apparatus in readiness, transfer 5 g of cuttings to the sulphur flask, and add about 5 g of  $\text{CaCO}_3$  or  $\text{Na}_2\text{CO}_3$ . With all stopcocks to the flask closed, add 70 ml of dilute HCl (1:1) to the funnel tube. Turn the stopcock to connect the flask with the test tube containing the sulphur absorbent, and open the stopcock on the funnel tube allowing the dilute HCl to flow slowly into the flask, until only 1 or 2 ml remain above the stopcock. Heat the flask gently at first till the acid is reacting energetically with the steel, then reduce the heat supply till the cuttings are dissolved, and increase it again at the end till the solution is boiling and steam has displaced all the gases in the flask. At this point turn the 3-way stopcock to connect the flask with the tube containing the bicarbonate solution, and cease heating the flask, which operations will cause the bicarbonate to be sucked back into the flask. Now disconnect the apparatus from the tube containing the sulphur absorbent and set the flask in cold water, causing more of the bicarbonate to flow back, and leaving the flask filled completely with  $\text{CO}_2$ . Finally, when the flask is cold, loosen the stopper, and pour in 6 ml of a mixture of 5 ml of starch and 1 ml of 8-per cent solution of KI. Replace the stopper, shake, remove the stopper entirely, and titrate immediately with the standard iodate or iodine solution to a faint blue end point. Subtract the blank and calculate the per cent

tin from the tin titer of the solution and the weight of sample taken.

To determine the blank, analyze in the same way a standard sample of steel, either free from tin or containing a known percentage, and containing approximately the same percentage of copper as the steel that is to be analyzed.

# Determination of Cobalt

## Methods Available

Cobalt added to steel produces properties similar to nickel. It is used mainly in high-speed tool steels, the alloy known as stellite, and in permanent magnet steels. However, its use in other steels may be extended. It is accurately determined gravimetrically or volumetrically by a number of methods known as the phosphate method, the cyanide method, the potassium nitrite method, the sulphide precipitation method, the electrolytic method, and the alpha-nitroso-beta-naphthol method.<sup>1</sup> Some of these methods are applicable only to steels of a certain composition. For example, the sulphide method is not conveniently applied to steels containing copper, which is now commonly met with in steel. Only the last two methods are considered sufficiently accurate for referee work and applicable to the more complex alloy steels. In the electrolytic method the cobalt is obtained on the cathode along with some sulphur and the nickel, from which it must be separated by dissolving in acid and determining nickel by usual methods and cobalt by the alpha-nitroso-beta-naphthol method. It is described in one of the references. Hence, the last has been selected for inclusion as a standard in this book.

Before the cobalt can be precipitated it must be separated from elements co-precipitated, and interfering substances must be excluded or side-stepped. Elements co-precipitated include Fe, Cu, Cr, Mo, Sn, Ti, V, W, and Zr. Nitric acid interferes as do also large proportions of nickel. The latter interference is overcome by reprecipitating, and the former can be excluded. Tungsten can be removed in the beginning, if the solution is carefully oxidized to leave chromium in the trivalent state, and all the other elements co-precipitated are separated with zinc oxide. For further details in connection with the zinc oxide separation see under *Chemical Separations*. A little cobalt may be held in the large precipitate of iron, which is ignored in routine work and recovered by dissolving in HCl and reprecipitating for referee work.

## Zinc Oxide-Alpha-Nitroso-Beta-Naphthol Method

### Special Reagents Required

Zinc oxide emulsion and a solution of alpha-nitroso-beta-naphthol are required. The emulsion is prepared as described under *Chemical Separations* and the *Determination of Manganese*, and the alpha-nitroso-beta-naphthol solution is made ready just before it is used by

dissolving 2 g of alpha-nitroso-beta-naphthol in 25 ml of glacial acetic acid.

A blank should be run with each determination, using a steel known to be free of cobalt.

### Procedure

**Solution of Sample and Separation with ZnO.**—Weigh 1 g or 2 g of the sample into a 400-ml beaker, dissolve in 50 ml concentrated hydrochloric acid and boil. When solution is complete, oxidize the iron and tungsten with about 5 ml of nitric acid added slowly and boil to the absence of fumes, or until the  $\text{WO}_3$  is a bright yellow. Evaporate to the first appearance of crystals. Dilute with 100 ml hot  $\text{H}_2\text{O}$ , digest, and cool the solution almost to room temperature. Add ammonia slowly while stirring until the precipitate of iron hydroxide formed dissolves with difficulty. Cool to room temperature and transfer with water to a 500-ml volumetric flask, unless all the solution is to be used, in which case it is not necessary to transfer it. Add slowly, with constant agitation of the flask, an emulsion of zinc oxide until an excess is present. As this point is approached the solution becomes milky and a slight amount in excess produces a heavy voluminous brown precipitate. Dilute to the mark with water and empty into a 600-ml beaker. Mix thoroughly by stirring. Let the precipitate settle, and, for a routine determination, decant 250 ml of the solution through a dry 12.5-cm filter paper of close texture into a 250-ml volumetric flask, ignoring a trace of zinc oxide that may pass through the paper. When 250 ml, representing 1 gram, have been filtered, transfer this solution to a 400-ml beaker and add 5 ml of concentrated hydrochloric acid.

For exact analysis, filter all the solution, wash 3 times with water, add 5 ml  $\text{HCl}$  to the filtrate, and evaporate. Transfer the paper and precipitate to the original beaker, and add 20 ml of  $\text{HCl}$  (1:1), rinsing the flask with the acid if the precipitation was not made in the original beaker. Thoroughly macerate the paper and add more acid if necessary to dissolve all the iron. Dilute to 200 ml and repeat the precipitation, combining filtrate and washings with that from the first precipitation. Then acidify and proceed as directed below.

**Precipitation of Cobalt.**—Heat the acidified solution to near the boiling point, adjust the volume to about 400 ml, and precipitate the cobalt with alpha-nitroso-beta-naphthol, which is prepared just before the solution is ready to precipitate by dissolving 2 g of alpha-nitroso-beta-naphthol in 25 ml of glacial acetic acid. Heat the reagent gently and add it to the hot hydrochloric acid solution containing the cobalt, 5 ml for each 0.01 g cobalt expected. The cobalt is precipitated as a red compound. A portion of the excess reagent also precipitates. Two grams of alpha-nitroso-beta-naphthol will precipitate 0.05 g or 5.0 per cent cobalt. If the percentage of cobalt is low, use a correspondingly smaller amount of the reagent.

Hold near the boiling point for 15 minutes, let settle, stir, and filter on an 11-cm ashless filter paper, using paper pulp. The last portion of the precipitate and reagent is removed from the sides of the beaker with difficulty. Wash the precipitate five times alternately with hot dilute hydrochloric acid (1:2) and hot water and finally 5 times with hot water. Ignite in a weighed silica or porcelain crucible at a very low temperature until the paper is gone, then at a higher temperature, but not above 900° C, for 30 minutes. If the sample contains much nickel, dissolve the oxide in HCl, reprecipitate the cobalt, ignite, cool, and weigh. The increase in weight of the crucible is cobalt oxide,  $\text{Co}_3\text{O}_4$ . If the steel contains much molybdenum or copper, dissolve and determine these elements by color, afterwards calculating Mo to  $\text{MoO}_3$ , and Cu to CuO. Subtract the proper blank and corrections, multiply the difference by  $100 \times 0.7343$ , and divide by the weight of sample used or represented by the oxide to find the per cent cobalt.

The ignited oxide does not have the exact formula  $\text{Co}_3\text{O}_4$ , and goes slowly to CoO above 900° C. If the weight of oxide is appreciable, it is, therefore, advisable to change the oxide to metallic cobalt by repeated ignition in hydrogen in a Rose-form crucible until the weight is constant.

### Volumetric Method

#### Direct Titration of Cobalt and Nickel with Potassium Cyanide

This method represents a revision of our former method (See *Sampling and Analysis of Alloy Steels*, page 60), and has been successfully applied not only to various synthetic solutions of steel and solutions of cobalt salts, but also with cobalt high-speed steel, and other high-alloy steels containing up to 12 per cent chromium, and about 0.5 per cent each of cobalt, molybdenum, and vanadium. The method of titration depends upon the same principles as explained under the corresponding method for nickel, with the substitution of the following reaction between cobalt nitrate and potassium cyanide.



#### Special Solutions Required

A standard solution of silver nitrate and of potassium cyanide are required, and these are the same as those used in the corresponding method for nickel in which 1 ml of the silver nitrate is equivalent to 0.1 per cent nickel on a sample of 1 g. Solutions based on cobalt are given at the end of this section.

The ammonium citrate-sulphate solution is also the same as that used for nickel.

### Procedure

Transfer 1 g of sample to a 400-ml beaker, add 35 ml of dilute sulphuric acid (1:6), heat gently till the steel is dissolved, and add 20 ml of dilute nitric acid (sp. gr. 1.20). Boil 20 minutes, add 25 to 50 ml of water, and filter, if necessary to clear the solution. Discard the residue.

To the clear solution add 15 ml of concentrated ammonia, stir, and dissolve any precipitate formed by adding nitric acid dropwise. Cool to room temperature or below and add 50 ml of ammonium citrate-sulphate solution. Carefully add dilute ammonia (1:1) until the solution barely turns red litmus to purple—not a deep blue. Dilute to 250 ml, add 10 ml of concentrated ammonia and 10 ml of an 18-per cent solution of ammonium acetate. Heat to boiling and boil 10 to 12 minutes. Cool, and if the cold solution does not smell faintly of ammonia, add 5 ml and boil for a shorter period. To the cold faintly ammoniacal solution, add 3 ml of concentrated ammonia and 3 ml of a 10-per cent solution of potassium iodide, and titrate as follows:

Add about 1 ml of the standard silver nitrate solution from a burette, noting the reading, and titrate with the standard potassium cyanide solution until the turbidity is dispelled, then add 1 ml of the latter in excess. Now add the silver nitrate carefully and finally dropwise until a faint turbidity appears, which is taken as the end point.

Multiply the ml of potassium cyanide used by the factor to convert this solution to equivalent of standard silver nitrate. Deduct the total number of ml of the standard silver nitrate used, and multiply this difference by the nickel titer, usually 0.1 per cent nickel on 1 g sample. This result gives the nickel equivalent to both the nickel and the cobalt in the sample. To find the per cent cobalt, deduct the per cent nickel present as found by the dimethyl glyoxime method and multiply by 0.804.

### Solutions Required

#### Standard Silver Nitrate Solution

Silver Nitrate .....	7.2024 g
Water to make .....	1000 ml
One ml of this solution equals 0.1 per cent cobalt on 1 g of sample.	

#### Standard Potassium Cyanide Solution

Potassium Cyanide .....	5.6 g
Potassium Hydroxide .....	1.0 g
Water .....	1000 ml

The silver nitrate solution is carefully prepared and the cyanide solution adjusted to exact agreement therewith. For this purpose, to a 400-ml beaker, containing 100 ml of water, 3 ml of ammonia and 2 ml of potassium iodide solution (10-per cent), there is added from a burette 30 ml of silver nitrate solution. Next, standard potassium cyanide solution is added until the solution is perfectly clear. Silver

nitrate solution is then added until a faint cloudiness appears, which is dispelled by 2 drops of potassium cyanide solution. The volume of the cyanide solution required is noted, and the cyanide solution is adjusted so that the standard solutions are in exact agreement. With exactly agreeing solutions, each milliliter excess of standard cyanide solution over the silver nitrate solution corresponds to 0.1 per cent of cobalt. The value of the solutions is then confirmed by titrating a standard cobalt steel, the cobalt content of which has been determined by one of the previously described gravimetric methods.

The percentage of nickel, as found by the dimethyl glyoxime method, is multiplied by 8.04 and deducted from the difference in ml between the cyanide and the silver nitrate solutions used; the difference is the cyanide equivalent to the cobalt, which divided by 10, gives the percentage of cobalt.

### The Determination of Small Percentages of Cobalt as in Plain-Carbon Steels

#### Procedure for Cobalt Under 0.10 Per Cent

Dissolve one or two 10-g portions of the sample in HCl, cautiously oxidize the iron with nitric acid, and separate most of the iron and all of the molybdenum with ether as directed under *Chemical Separations*, but wash the ether extract once with a little dilute hydrochloric acid (sp. gr. 1.1). Heat the acid solution gently to expel ether, add potassium chlorate, and boil to thoroughly oxidize the solution. If more than one portion was used, combine the solutions at this point.

Dilute the solution to 200 ml, make a double separation with zinc oxide, and complete the determination as directed in the zinc oxide-alpha-nitroso-beta-naphthol method.

If nickel is absent or present also in small percentages, the cobalt may be titrated with silver nitrate and potassium cyanide.

#### Text References

1. "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Alloy Steels," 2nd Ed., p. 58.
2. Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel," 1st Ed., p. 334; New York, John Wiley and Sons, Inc., 1931.



# Determination of Tungsten

## Use of Tungsten and Methods for its Determination

While tungsten is generally associated with tool steels, to which it is added in proportions up to 20 per cent, it is also used as an alloy in other steels, in which it may be found in proportions varying in the extreme from 0.20 per cent to 12 per cent. Solution of these steels is most easily effected in dilute HCl or  $\text{H}_2\text{SO}_4$ , which leaves a little of it in solution, and the remainder as insoluble metallic tungsten and tungsten carbide, both readily oxidized to yellow tungstic acid,  $\text{WO}_3$ , by nitric acid, or sodium or potassium chlorate. The separation is more nearly complete when the tungsten exceeds 1 per cent, and when this amount is present, that which remains in solution can be precipitated by the addition of an alkaloid such as cinchonine,  $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}$ . As an alternative, a portion of a high-tungsten steel sufficient to increase the tungsten of the mixture to more than 1 per cent has been added to the steel sample to be analyzed. Tungstic acid so precipitated is somewhat contaminated, mainly by silica, but also by Fe and by such elements as Cr, Cb, Mo, P, Sn, Ta, Ti, V, and Zr, if any of these are present. Purification of the tungstic acid, therefore, forms the chief problem in the analysis. The following procedures provide for the removal of most of the impurities, but are open to the objection that the several errors in determining the impurities are all thrown on the tungsten. Hence, the accuracy depends largely upon the composition of the steel. In many cases, silicon can be obtained accurately by the same treatment as is necessary in the purification of the tungsten, and the methods provide for this determination, also. Besides, methods are given for checking the results for silicon and for tungsten, when the latter is present in proportions under 0.2 per cent.

### Weight of Sample

The weight of sample used is varied according to the percentages of silicon and tungsten present. For high-speed steels 1 g is used, and silicon and tungsten are determined on separate samples. The 2 elements are also determined on separate samples when the tungsten is under 1 per cent, 4 g or 5 g being used for tungsten and the most convenient factor weight for silicon. For tungsten between 8 per cent and 10 per cent, either 2 g may be used or the factor weight for silicon, 2.336 g; for tungsten between 1 per cent and 8 per cent, either 4 g or the factor weight for silicon, 4.672 g.

When the tungsten present is below 1 per cent and the time for an

analysis is limited, 5 g of sample are used and a portion of an authoritative standard sample of tungsten steel may be added to increase the tungsten present and the completeness of the separation.

### Method for Checking Silicon Results

For checking the silicon result by any of the methods given in this section, the following procedure is recommended as the quickest and most accurate.

**Special "Phosphodant" Solution Required.**—Mix 300 ml of perchloric acid (68- to 72-per cent) with 600 ml of orthophosphoric acid (85-per cent). Keep in a cool place, and never set on a shelf elevated above the work table.

**Procedure.**—Weigh and transfer 2.336 g of sample to a 400-ml covered beaker. For high-speed steels, add 40 ml of the "phosphodant" solution, decreasing the amount with the tungsten to 25 ml for steels containing less than 2 per cent tungsten. Apply heat gradually until the steel dissolves and no dark particles remain (20 to 35 minutes). Add 30 ml of perchloric acid (70-per cent), and heat on a ring of asbestos, keeping the acid condensing on the wall of the beaker for 10 minutes. Cool, add 100 ml of water, stir, and filter through a fairly close paper. Ignite in a clean platinum crucible and weigh as impure silica. Moisten the residue with dilute sulphuric acid (1:1), add several ml of hydrofluoric acid (48-per cent), evaporate in an air bath, ignite gradually, cool, and weigh again. Subtract the second weight from the first and multiply the difference by 20 to find the per cent silicon.

### HCl-HNO<sub>3</sub>-Cinchonine-Na<sub>2</sub>CO<sub>3</sub> Fusion Method for Silicon and Tungsten or Tungsten Alone

#### Special Solutions of Cinchonine Required

For use in precipitating, dissolve 25 g of cinchonine in 200 ml of dilute HCl (1:1). For a wash solution dilute 30 ml of the precipitating solution to 1 liter.

#### Procedure for All Steels except High-Speed Steels

Transfer the sample to a 400-ml beaker or casserole having a smooth unetched surface. Cover the container, add 75 to 100 ml of HCl, according to the weight of sample used, heat to incipient boiling, and keep the volume constant by additions of water. Oxidize the tungsten by one of the following methods:

**A. Absence of Much Vanadium, Silicon Desired.**—To the hot solution add HNO<sub>3</sub> dropwise, until the solution is completely oxidized, and add 5 to 10 ml excess. Evaporate to dryness and bake at 120° C, if both silicon and tungsten are required, then take up with HCl and repeat the evaporation. If only W is required, evaporate to a paste,

take up in dilute HCl, and again evaporate to a paste. Take the residue up in 60 ml HCl (1:1), digesting until the soluble portion dissolves. Then add 2 drops  $\text{HNO}_3$ . Add 100 ml hot water, 5 ml cinchonine solution, and boil a few minutes until the  $\text{WO}_3$  is clean and yellow. After the  $\text{WO}_3$  has settled, filter through a close filter paper, if the tungsten present exceeds 2 per cent. If less tungsten is present, let the solution stand 18 to 24 hours before filtering.

**B. Presence of Much Vanadium, Silicon Not Desired.**—To reduce the proportion of vanadium held by the tungstic acid, oxidize the iron and tungsten with hydrogen peroxide instead of nitric acid. Cool the solution to about  $70^\circ \text{C}$ , and add a solution of 30-per cent hydrogen peroxide (Perhydrol) in 17 ml of water with constant stirring. Then boil the solution down to a volume of about 25 ml, dilute to 200 ml with hot water, and proceed by either of the two following plans:

(a) Stir in 5 ml of cinchonine solution, boil a few minutes, and let the beaker stand until all the tungsten has precipitated (18-24 hours), if little is present.

(b) Add slowly with constant stirring, a saturated solution of sulphur dioxide until the ferric chloride is all reduced to the ferrous state. Heat to boiling, cool somewhat, add 5 ml of cinchonine solution, boil, and let the beaker stand until the precipitate separates (1 to 3 hours if tungsten is low).

Put  $\frac{1}{4}$  of a paper (11-cm) that has been macerated in hot water in the apex of the filter paper. Filter the solution and wash the filter with hot HCl (1:4), which contains 10 ml of cinchonine solution per liter. Wash once with hot water, reserving the filtrate for test later if the presence of Cb is suspected. If any  $\text{WO}_3$  adheres to the beaker, wipe it off with a small piece of paper moistened with  $\text{NH}_4\text{OH}$ , and then add this to the main  $\text{H}_2\text{WO}_4$  precipitate. Transfer to a platinum crucible. Ignite the precipitate at a dull red at first, and finally, at  $800^\circ$  to  $850^\circ \text{C}$ . Weigh, and record the total weight as the weight of the crucible +  $\text{WO}_3$  +  $\text{SiO}_2$  + impurities. Cover the residue with HF. Add 2 drops concentrated  $\text{H}_2\text{SO}_4$ . Evaporate slowly to dryness until all white fumes are driven off. Ignite at a full red heat as before. Weigh and record the weight lost as the total weight of the  $\text{SiO}_2$ . If silicon is desired and a factor weight was not used, calculate the silicon, thus:

$$\frac{\text{Wt. SiO}_2 \times 0.4672 \times 100}{\text{Weight of Sample}} = \text{Per cent Si}$$

Record the gross weight now as the weight of the crucible + tungsten + impurities. Add to the crucible sodium carbonate, or, in the absence of titanium, sodium-potassium carbonate equal to about 10 times the weight of the residue. Use only carbonate known to give no blank; otherwise determine the blank with care. Fuse completely and dissolve the fusion in 100 ml hot water. Filter through a No. 42

Whatman or similar close-textured paper, and wash with hot water. Ignite the filter and residue and weigh. In the absence of much Cr, Mo, V, or Cb, record the weight now as the weight of the crucible + impurities, and the difference between these last two weights as pure  $\text{WO}_3$ .

$$\text{Per Cent W} = \frac{\text{WO}_3 \times 0.7931 \times 100}{\text{Weight of Sample}}$$

If both tungsten and columbium are present in the sample, and the difference in the weights is small, it represents  $\text{WO}_3 + \text{Cb}_2\text{O}_5$ , and it is not likely that all of either element is recovered. In this event, test the filtrate as follows:

Acidify the solution with  $\text{HCl}$ , adding 4 per cent excess. Boil 10 minutes, when nearly all the columbium will be precipitated, dragging with it much of the tungstic acid. If columbium is absent, no precipitate will be obtained. For the separation of tungstic and columbic acids, refer to the methods for columbium.

#### Perchloric Acid-Cinchonine-NaOH Solution Method

##### Special Cinchonine Solutions Required

For precipitating, dissolve 25 g cinchonine in 200 ml of dilute hydrochloric acid (1:1). For washing, dilute 30 ml to 1 liter.

##### Procedure

Transfer the sample, 2.336 g, if W is under 3 per cent, and 1.168 g if it is over, to a 400-ml beaker and dissolve in 60 ml 1:1  $\text{HCl}$ . When solution is completed, add  $\text{HNO}_3$  dropwise until iron is oxidized, boil for a few minutes, and add 25 ml  $\text{HClO}_4$  (70-per cent). Evaporate to fumes of perchloric acid and continue fuming for 2 or 3 minutes. Cool, add 150 ml  $\text{H}_2\text{O}$  and 25 ml  $\text{HCl}$  (1:1), and bring to a boil. Add 5 ml cinchonine solution and digest for 30 minutes or longer at  $90^\circ$  to  $95^\circ \text{C}$ .

Filter on a tight ashless paper, washing well with cinchonine wash solution. Dissolve the small amount of W which cannot be scrubbed from the beaker with a little  $\text{NH}_4\text{OH}$  and evaporate to dryness. After bringing into solution with 1:1  $\text{HCl}$ , add a few drops of cinchonine solution, bring to a boil, and pour the solution through the filter. Transfer the filter to a weighed platinum crucible and ignite at as low a temperature as possible until the carbon is consumed. Cool and weigh as  $\text{SiO}_2$  + impure  $\text{WO}_3$ . Treat with 2 drops  $\text{H}_2\text{SO}_4$  (1:1) and 3 to 5 ml  $\text{HF}$ . Evaporate carefully to dryness on a sand bath, ignite at  $750^\circ$  to  $850^\circ \text{C}$ , cool, and weigh again as impure  $\text{WO}_3$ .

Dissolve the impure  $\text{WO}_3$  in the crucible with 15 ml of a 10-per cent solution of  $\text{NaOH}$ , transfer to a small beaker, and dilute with  $\text{H}_2\text{O}$  to 75 ml. Filter on a small ashless paper, wash well with hot water,

and discard the filtrate. Dissolve oxides from the paper, into the beaker, with hot 1:1 HCl. Precipitate with  $\text{NH}_4\text{OH}$ , boil, and refilter, washing well with hot  $\text{H}_2\text{O}$ . Ignite and weigh the residue, the weight of which subtract from the weight of impure  $\text{WO}_3$ .

The difference between the weight of  $\text{SiO}_2$  + impure  $\text{WO}_3$  and the weight of impure  $\text{WO}_3$ , multiplied by 40, represents the percentage of Si if 1.168 g sample was used. If 2.336 g sample was taken, multiply the difference in weight by 20 to obtain per cent Si.

The difference between the weight of crucible and the corrected weight of  $\text{WO}_3$  multiplied by the factor  $0.679 \times 100 =$  per cent W, if a 1.168 g sample is used. For a 2.336 g sample, the factor is 0.3395. Finally, correct the result for any addition, if tungsten was added to increase the amount present.

### Alpha-benzoinoxime Method for Low Tungsten

As a means of checking results for tungsten when present in small percentage, the following procedure is used. The method was first announced by the National Bureau of Standards in Research Paper 453.<sup>1</sup>

#### Special Solution Required

**Alpha-benzoinoxime (2-per cent).**—Dissolve 10 g of the special reagent in 500 ml of ethyl alcohol, and filter through glass cotton, if not clear.

**Washing Solution.**—Add 10 ml of  $\text{H}_2\text{SO}_4$  to 1 liter of water and cool. Just before using cool to  $10^\circ \text{C}$  and mix in 50 ml of the alpha-benzoinoxime solution.

#### Procedure

Weigh and transfer 5 g of sample to a 600-ml beaker. Add 75 ml of dilute sulphuric acid (1:6), heat gently until solution is effected, and add slowly just enough dilute nitric acid (sp. gr. 1.20) to oxidize the iron and decompose carbides. If not already present, add 5 mg of molybdenum, preferably in the form of a soluble salt such as sodium molybdate. Dilute to 150 ml, cool to  $5^\circ \text{C}$ , and stir in slowly 10 ml of alpha-benzoinoxime solution. Stir 5 minutes, add 5 ml more of the same solution, and let the beaker stand in the cooling mixture for 10 minutes, stirring occasionally. Filter with paper pulp through a close filter, refiltering the first runnings, if cloudy. Wash with the special washing solution, and transfer the paper to a weighed platinum crucible. Char and ignite to constant weight at  $525^\circ \text{C}$ . Weigh as impure  $\text{MoO}_3 + \text{WO}_3$ . Dissolve by digesting with dilute ammonia (1:9), filter through a small close paper, and wash with 1-per cent ammonia water. Reserve the filtrate and ignite the paper as before. Then subtract to find the weight of the pure oxides,  $\text{MoO}_3 + \text{WO}_3$ .

Determine molybdenum in the ammoniacal solution of the oxides, by acidifying with  $\text{H}_2\text{SO}_4$ , precipitating twice with  $\text{H}_2\text{S}$ , igniting, and weighing as  $\text{MoO}_3$  to find tungsten by difference.

Or, if tungsten is very low, determine molybdenum by color, calculate to  $\text{MoO}_3$ , and find tungsten by difference.

### Volumetric Method for Low Tungsten

The following procedure was suggested by T. R. Cunningham, and is given in full by Lundell, Hoffman, and Bright.<sup>2</sup>

#### Procedure

Transfer 2 g to a platinum dish, cover, and dissolve with 30 ml  $\text{HCl}$  and 0.5 ml  $\text{HF}$  at  $60^\circ$  to  $70^\circ$  C. Boil 5 minutes, add slowly 1 to 2 ml  $\text{H}_2\text{O}_2$  (30-per cent) and 20 ml of saturated solution of  $\text{H}_3\text{BO}_3$ . Boil 2 minutes, dilute to 100 ml, add  $\text{H}_2\text{SO}_4$  to a light straw color, cool rapidly, add 10 ml cinchonine solution and paper pulp, stir and let stand 15 minutes. Filter through a close paper, wash with dilute cinchonine wash solution, then with 2-per cent  $\text{KNO}_3$ . Transfer the paper to a 300-ml Erlenmeyer flask, add 10 ml  $\text{H}_2\text{O}$  and an excess of 0.02  $N$   $\text{NaOH}$  solution, macerate the paper, and back-titrate with 0.02  $N$   $\text{HCl}$  solution using phenolphthalein solution. Find the ml of  $\text{NaOH}$  solution required to neutralize the  $\text{H}_2\text{WO}_4$ , multiply by 0.00184 and by 100, and divide by 2 to find the per cent tungsten.

#### Procedure for Determining Tungsten in High-Speed Steels

Transfer 1 g of drillings to a covered 250-ml beaker, add 50 ml of  $\text{HCl}$ , and heat to incipient boiling. Place the beaker on a warm spot, add a few drops of  $\text{HNO}_3$ , and wait until the vigorous action subsides. The addition of  $\text{HNO}_3$  results in the momentary formation of brown ferric compounds which are quickly reduced again with the production of unstable dark green compounds. When this change takes place, repeat the treatment with  $\text{HNO}_3$  until it ceases to recur. In this way, all the iron is oxidized with the production of a perfect solution of it and the tungsten and with the use of very little more  $\text{HNO}_3$  than is required for the oxidation of the iron only. Evaporate the liquid as quickly as possible until tungstic oxide begins to separate and then add 10 ml of cinchonine solution (see page 237), afterwards boiling more slowly until the volume is reduced to 20 ml. Add then 100 ml of hot water and set aside for at least 15 minutes.

Filter through paper pulp, wash with 5-per cent  $\text{HCl}$  and water; or preferably with cinchonine solution diluted with 30 to 35 parts of water. Dry and ignite in a platinum crucible; remove the silica with  $\text{HF}$  alone, ignite again, and weigh. Cover the residue with about twice its weight of dry sodium carbonate and place the crucible in the hottest part of the muffle for 5 minutes. Remove the crucible from the

muffle and when the fused mass is cold, extract with hot water and filter. Ignite the washed residue in the same crucible. The loss in weight is tungstic oxide.

Weight of  $\text{WO}_3 \times 0.7931 \times 100 =$  per cent tungsten.

#### Text References

1. National Bureau of Standards Journal of Research, Research Paper 453, 9, No. 1, January, 1932.
2. Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel," page 331. New York, John Wiley and Sons, Inc., 1931.

# Determination of Uranium

## Occurrence of Uranium and Methods Available

Uranium has been added to certain highly alloyed steels, such as the high-speed steels. In other steels it has not been used very extensively. However, small percentages of uranium and the rare earth, cerium, may be encountered by the chemist at any time. Uranium compounds can be reduced with zinc and reoxidized with  $\text{KMnO}_4$  solution, facts that have led to many attempts to develop volumetric methods for its determination, but many difficult separations are necessary to separate it completely from the many other reducible elements, such as iron, chromium, molybdenum, vanadium, tungsten, and the like. It is somewhat easier to obtain it in a form that can be ignited to the oxide  $\text{U}_3\text{O}_8$ . The few methods that have been found most satisfactory are given below:

### Procedure Dissolving the Sample in Sulphuric or Hydrochloric Acid with Final Precipitation with Cupferron

#### I. A. Solution in Sulphuric Acid

For uranium over 0.1 per cent, transfer 5 g to a 300-ml Erlenmeyer flask and add 100 ml of dilute  $\text{H}_2\text{SO}_4$  (1:9). For uranium under 0.1 per cent, use 10 g and 150 ml of the acid. Cover the flask and heat gently till solution is complete. Filter the solution into a 500-ml Erlenmeyer flask, and wash the filter and residue, which contains some of the uranium, with 1-per cent  $\text{H}_2\text{SO}_4$ . Stopper the flask to exclude air, set it aside, and treat the residue by one of the following methods, using the second if the residue is large, whether tungsten is known to be present or not.

(a) **Treatment of Residue in the Absence of Tungsten.**—Transfer the paper and residue to a platinum crucible, and dry and ignite it slowly in a muffle with the cover removed from the crucible, until all the paper has been burned and carbides converted to oxides. Cool, add 5 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) and 5 to 10 ml of  $\text{HF}$  (48-per cent), and evaporate carefully till dense fumes are evolved. Cool, dilute carefully, and add the solution to the reserved filtrate.

(b) **Treatment of Residue in the Presence of Tungsten.**—Transfer the filter and residue to the original flask, add 25 ml of  $\text{HCl}$  and an equal volume of  $\text{HNO}_3$ , and shake or stir to disintegrate the paper. Heat until the paper is destroyed and  $\text{H}_2\text{WO}_4$  is yellow, if tungsten is present, adding more  $\text{HNO}_3$  as may be necessary, and 10 ml of  $\text{H}_2\text{SO}_4$ ,



after the tungsten is oxidized. Cool the fuming solution, add 200 ml of water, and heat to incipient boiling. While shaking, add ammonia until there is a considerable excess present, and boil for 10 minutes to dissolve the tungstic oxide. Filter, wash with 5-per cent ammonia, and discard the filtrate. Dissolve the precipitate in 50 ml of hot dilute HCl (1:3), dilute to 150 ml, add an excess of ammonium carbonate, heat gently for 5 minutes, add more of the carbonate, and filter. If the precipitate is large, dissolve with HCl and repeat the treatment. Acidify the filtrate, which contains the uranium, and boil to expel  $\text{CO}_2$ . Add an excess of ammonia, boil, and filter. Dissolve the precipitate, which contains the uranium, in dilute  $\text{H}_2\text{SO}_4$  (10-per cent) and add it to the solution from the ammonia separation below.

**I. B. Solution in Hydrochloric Acid.**—Weigh 5 g of sample and transfer it to a 600-ml beaker. Add 100 ml of dilute HCl (1:1) and heat gently until the metal is dissolved. Add  $\text{HNO}_3$  dropwise to oxidize the iron and tungsten, if the latter is present, and then add 10 ml more. Digest to destroy carbides or till the tungstic acid is a bright yellow, but do not evaporate, and add water to keep the volume at 100 ml. Filter with the aid of paper pulp and wash with dilute HCl (5-per cent). Start the filtrate evaporating and rinse the precipitate, if tungstic acid, into the original beaker, being careful not to puncture the paper. Add 10 ml of ammonia, which must be free of carbonate, and boil for 5 minutes. Pour this ammoniacal solution through the paper, and wash the beaker and paper thoroughly with warm water. Discard the filtrate, dissolve the residue on the filter with hot dilute HCl (1:1), and add it to the filtrate that is evaporating. Evaporate the combined solutions to a syrup, add 25 ml HCl, and again evaporate. Dilute, filter, wash with dilute HCl, and evaporate a third time.

## **II. A. Separation of Uranium, etc., with Ammonia**

### **Following Solution in $\text{H}_2\text{SO}_4$**

Dilute the original filtrate to 250 ml, and add dilute ammonia (1:1) with constant shaking until a permanent precipitate is formed and an excess of 2-3 ml is present. Heat to boiling, filter through a 15-cm paper, and wash 3 or 4 times with hot water. Discard the filtrate and transfer the paper and precipitate to the flask in which the precipitation was made. Add 200 ml of dilute  $\text{H}_2\text{SO}_4$  (1:9) and heat till the precipitate has dissolved. Add the solution from treatment of the residue, if it has not already been added, and reserve the solution for the separation with cupferron as directed below.

**II. B. Separation of Iron with Ether.**—Add 20 ml of hydrochloric acid (sp. gr. 1.19), heat gently, but do not boil, and separate most of the iron and all of the molybdenum with ether as directed under *Chemical Separations*. Discard the ether layers, and evaporate the acid solution just to dryness, but do not bake. Add 20 ml of  $\text{H}_2\text{SO}_4$

dilute to 200 ml, and treat for the separation of uranium, etc., with cupferron as directed below.

### III. Separation with Cupferron

To the sulphuric acid solution, prepared by either of the methods above, add 5 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and boil vigorously for 10 minutes to oxidize iron, chromium, uranium, etc., and destroy the excess persulphate. Cool to  $15^\circ\text{C}$ , adjust the volume to 200 ml, and stir in a cold 6-per cent solution of cupferron. Filter, wash with cold 1-per cent  $\text{H}_2\text{SO}_4$  containing a little of the cupferron solution, and discard the precipitate.

Evaporate the filtrate and washings with 20 ml of  $\text{HNO}_3$  to fumes, repeating, if necessary, to destroy all organic matter. Cool and measure the solution to gain an idea of the acid present for use later. Dilute to 200 ml, add 3 g of pure zinc, free from any impurity precipitated by cupferron, cool to  $15^\circ\text{C}$ , and filter through a close paper. Stir the solution for 1 minute and dilute to give a volume containing 6 per cent  $\text{H}_2\text{SO}_4$ . Add some paper pulp, and precipitate the uranium by adding cupferron as before. Filter, wash with 4 per cent  $\text{H}_2\text{SO}_4$  containing 1.5 to 2 g of cupferron per liter, and transfer the filter and precipitate to a weighed platinum crucible. Dry and ignite carefully and gradually until organic matter is decomposed and then heat to constant weight at  $1000^\circ\text{C}$ . Cool and weigh as  $\text{U}_3\text{O}_8$ , multiply by  $100 \times 84.81$ , and divide by the weight of sample used to find the per cent uranium.

### Procedure Dissolving the Sample in Hydrochloric Acid with Final Precipitation with Ammonia

#### Solution of Sample and Separation of Tungsten

Transfer 3 g of the sample to a 400-ml beaker, add 40 ml of dilute  $\text{HCl}$  (sp. gr. 1.13), and heat gently till the cuttings are dissolved. Add, slowly at first, 10 ml of  $\text{HNO}_3$ , and evaporate slowly to dryness. Add 20 ml of dilute  $\text{HCl}$  (1:1), dilute with 40 ml of water, and boil 5 minutes. Filter and wash with dilute  $\text{HCl}$  (1:9).

If much tungsten is present, treat the residue for the recovery of uranium as directed in the preceding method.

#### Separation with Ether

Boil the filtrate and washings, which contain all the uranium, until the volume is about 20 ml. Cool and separate most of the iron with ether as directed under *Chemical Separations*, aiming to leave in the acid solution iron equal to at least 5 times the amount of vanadium present.

**Separation of Manganese.**—Evaporate and boil the acid solution from the ether extraction down to 10 ml and add 30 ml of  $\text{HNO}_3$ .

Repeat these operations to expel all the HCl. On the last evaporation to 10 ml, add 40 ml of  $\text{HNO}_3$ , heat, and then add 5 g of sodium chlorate to oxidize chromium and precipitate the manganese. Boil down to 20 ml, and filter on an asbestos plug, washing the filter with colorless nitric acid and finally, 1 or 2 times with hot water.

### Separation with Ammonia

Dilute the filtrate to 200 ml and add an excess of ammonia free of carbonate. Boil, filter, and wash with water. If chromium has not been removed, dissolve the precipitate with dilute nitric acid (sp. gr. 1.20) and repeat the treatments with  $\text{HNO}_3$  and  $\text{NaClO}_3$  and ammonia.

### Separation with Ammonia and Sodium Carbonate

Dissolve the final precipitate from the ammonia separation with dilute  $\text{HNO}_3$  (sp. gr. 1.20). Neutralize the solution with ammonia and add 20 ml excess. Heat to boiling, remove from the heat, and carefully add 2 g of  $\text{Na}_2\text{CO}_3$  while stirring constantly. Boil 2 minutes, again add 2 g of  $\text{Na}_2\text{CO}_3$ , stir, and boil for  $\frac{1}{2}$  minute. Let the precipitate of iron and vanadium settle, then filter, dissolve the precipitate with dilute  $\text{HNO}_3$  and repeat the separation to recover traces of uranium.

### Final Precipitation of Uranium with Ammonia

Combine the filtrates from the carbonate separations, acidify with HCl, and boil to expel  $\text{CO}_2$ . Add an excess of ammonia free from carbonate and boil for 5 or 6 minutes. Let the precipitate of uranium hydroxide settle, collect it upon a filter, and wash with freshly boiled water containing a little ammonia free of  $\text{CO}_2$ . Dissolve the precipitate with dilute  $\text{HNO}_3$  (sp. gr. 1.20) and repeat the precipitation, keeping the volume under 50 ml. Filter, wash as before, ignite gradually to constant weight in a weighed platinum crucible, and weigh as possibly impure  $\text{U}_3\text{O}_8$ .

Dissolve the oxide in a little dilute  $\text{HNO}_3$  (sp. gr. 1.20), filter, and wash the filter with water. Ignite the filter as before and subtract the weight of iron and chromium oxides from the weight of the impure  $\text{U}_3\text{O}_8$ . In the filtrate, determine vanadium by adding  $\text{H}_2\text{O}_2$  and comparing the color developed with that of a standard. Calculate V in grams to  $\text{V}_2\text{O}_5$  and subtract.

Consider the difference pure  $\text{U}_3\text{O}_8$ . Multiply by  $100 \times 84.81$  and divide by the weight of sample to find the per cent uranium.

## Determination of Zirconium

When added to steel, zirconium acts chiefly as a deoxidizing agent, combining, it is thought, with oxygen, nitrogen, and sulphur, forming with the last a compound insoluble in hydrochloric acid. Occasionally it is added as an alloying element. It, therefore, may be present in very small or in relatively large proportions, when present at all.

### Methods Available

In all methods the element is determined gravimetrically, being obtained and weighed as the phosphate,  $\text{ZrP}_2\text{O}_7$ , or the oxide,  $\text{ZrO}_2$ . It is always accompanied by the rarer element hafnium, from which it can be separated only by a tedious physico-chemical procedure, but since the association is in the ratio of about 100 Zr to 1 Hf, the results obtained by simple chemical procedures for steel and most of the iron alloys may be considered as zirconium. With the ordinary reagents, zirconium reacts like aluminum, titanium, columbium, or tantalum, from the last three of which it is difficult to separate completely. Tin, which has become a somewhat common impurity in ordinary steel, must also be considered. In the complex alloy steels, it may occur with one or more of these elements and with various combinations of others, such as As, Cr, Co, Cu, Mo, Ni, U, V, and W, besides the common elements Mn, P, and Si. Therefore, its exact determination in such steels has, until recently, been a difficult analytical problem. Now, however, several methods for its separation are available, and its determination no longer presents the problem that its interference in the determination of other elements does. These methods include, as initial steps, separations with ammonia, phenylhydrazine, ammonium phosphate, ether (followed by ammonium phosphate), cupferron, phenylarsonic acid, and selenious acid. The first two precipitate so many elements with the zirconium that they are seldom used, and the last is subject to many objections, not the least of which is the menace to the health of the analyst. Interesting facts associated with the three most reliable and convenient methods of separation are presented as follows:

**Precipitation with Diammonium Phosphate** in an approximately 10-per cent sulphuric or hydrochloric acid solution is one of the oldest methods to become outstanding. In such a strongly acid solution, only titanium, columbium, tantalum, and hafnium are completely precipitated with the zirconium, while the interfering elements are tungsten, chromium, and tin. Precipitation of titanium is prevented if it is peroxidized with hydrogen peroxide; and special measures must be taken

to avoid error by the others, if present. For example, to remove tin and tungsten the ignited phosphate precipitate is fused with  $\text{Na}_2\text{CO}_3$ ; for Cb and Ta with  $\text{KOH}$ ; the fusion is dissolved in water; the solution filtered, the residue ignited, fused with  $\text{K}_2\text{S}_2\text{O}_7$ , dissolved in acid, and Zr reprecipitated. Precipitations can be made in oxidized or reduced solution, and in the presence of all the iron, but are slow in oxidized solution, faster in reduced solutions, and most rapid and complete when most of the iron has been removed, as with ether.

**Precipitation with Cupferron (Nitrosophenylhydroxylamine,  $\text{C}_6\text{H}_5\text{N} \cdot \text{NO} \cdot \text{OH}_4$ ) in Reduced Acid Solution** has become a standard procedure. Under these conditions Cb, Sn, Ta, Ti, U, and V are completely precipitated with the zirconium, and some of the Fe, with traces of Cu, W, and Mo, will be carried down to contaminate the precipitate. Following the initial separation, the ignited precipitate is fused with  $\text{K}_2\text{S}_2\text{O}_7$ , and the Zr is reprecipitated as phosphate in sulphuric acid solution containing  $\text{H}_2\text{O}_2$ , which prevents co-precipitation of Ti. If Cb, Sn, Ta, or W are present, the zirconium phosphate precipitate must be purified as described above.

**Precipitation with Phenylarsonic Acid [ $\text{C}_6\text{H}_5\text{AsO}(\text{OH})_2$ ]** is the most recent, also the simplest and most accurate of the methods yet discovered for zirconium. In 10-per cent  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  solution of a zirconium compound, the reagent precipitates white flocculent  $\text{ZrO}(\text{C}_6\text{H}_5\text{AsO}_3)_2$ , which, however, may vary in composition when precipitated under different conditions. It is converted to  $\text{ZrO}_2$  by igniting, treating with  $\text{HF}$  and a little  $\text{H}_2\text{SO}_4$ , fuming, and reigniting at  $1000^\circ \text{C}$ . Iron, if present in large percentages, contaminates the precipitate, and is separated with ether to avoid a double separation with phenylarsonic acid. Titanium does not interfere if  $\text{H}_2\text{O}_2$  is present when the precipitation is made nor do Al, Cr, Mo, or V in proportions found in alloy steels. Tin is precipitated very slowly and tungsten is bothersome. If the latter is present, it should be removed at the beginning by oxidizing to  $\text{WO}_3$  and filtering. To recover Zr, the  $\text{WO}_3$  is dissolved with ammonia and the residue remaining is dissolved in hot  $\text{HCl}$  and added to the filtrate from the tungsten. The method requires less than half as much time as the cupferron method, and is otherwise more convenient.

The various procedures based upon these separations, which have been found to give satisfactory results when properly applied, are given in the methods that follow:

### Methods Depending Upon Separating and Weighing Zirconium as Phosphate

#### Direct Perchloric Acid-Phosphate Method

For zirconium in plain-carbon and stainless steels, absence of columbium, tantalum, tungsten, and tin.<sup>3</sup>

**Procedure.**—Dissolve 10 g of the sample with 60 ml of HCl in a 500-ml beaker, oxidize with 15 ml of  $\text{HNO}_3$ , added slowly, and boil to the disappearance of red fumes. Add 2 g of diammonium phosphate and evaporate without boiling till iron salts form a pasty mass. Add 10 ml of perchloric acid (70-per cent), and continue the evaporation at a low temperature till copious fumes of perchloric acid are evolved. Take up with 50 ml of HCl, dilute to 400 ml, and stir in some paper pulp. Filter through a close, double, 12-cm filter paper, and wash with dilute hydrochloric acid (1:20) until washings tested with KCNS solution give a negative test for iron. Ignite in a platinum crucible, moisten the residue with 6 drops of  $\text{H}_2\text{SO}_4$ , and volatilize silica by adding 10 ml of HF and evaporating slowly to fumes. Cool, add water to dissolve iron salts, transfer to a small beaker, and add 0.25 g of diammonium phosphate to provide an excess of phosphate. Heat almost to boiling, filter, and wash 3 or 4 times with water. Ignite to constant weight in a weighed platinum crucible, and multiply by 3.439 to find the per cent zirconium in the sample.

#### Phosphate-Hydrogen Peroxide Method, Absence of Columbium, Tantalum, and Tin

Hexavalent titanium is not precipitated as phosphate. In this method, first suggested by Cunningham and Price,<sup>2</sup> its co-precipitation with the zirconium is prevented by treating with hydrogen peroxide prior to precipitating with diammonium phosphate.

**Procedure.**—Transfer 5 or 10 g of the sample (depending on the probable amount of zirconium present) to a 600-ml beaker, add 40 ml of HCl (sp. gr. 1.19) for a 5-g or 60 ml for a 10-g sample, and heat to between  $80^\circ\text{C}$  and  $90^\circ\text{C}$ . When action of the acid has ceased, add 8 ml or 15 ml of 30-per cent hydrogen peroxide (Perhydrol) diluted with 25 ml of water, to break up carbides, oxidize iron and tungsten, and peroxidize titanium. Continue heating the solution for 1 or 2 minutes, and if tungsten is present, as indicated by a yellow residue, continue to boil for 5 minutes. Then dilute with warm water to 350 ml, and proceed in either of two ways as follows:

If tungsten is present, it can be eliminated at this stage or permitted to remain to be removed later. To remove it and recover zirconium, filter the solution through a close paper, wash once or twice with hot water, and dissolve the  $\text{H}_3\text{WO}_4$  on the paper with ammonia. Transfer the paper to a beaker, add hydrochloric acid, and digest to dissolve any slight residue. If the residue is considerable, ignite the paper gently, digest with HCl, and if the residue does not dissolve, evaporate to dryness, fuse with a little acid sodium sulphate, and dissolve in dilute hydrochloric acid. Add this solution to the original filtrate.

Add dilute ammonia (1:1) till a permanent precipitate forms and follow with dilute HCl (1:1), dropwise, with constant stirring until

the precipitate just disappears. To reduce the iron, add 10 g or 20 g of sodium sulphite dissolved in 50 ml of hot water, follow with 20 ml of HCl, and stir for 1 minute. Dissolve 8 or 10 g of diammonium phosphate in 50 ml of water, pour the solution into the beaker, stir the mixture vigorously for at least 5 minutes, and digest for about 2 hours at a temperature of 70° C.

Filter the solution through a close 9-cm filter containing a little ashless paper pulp, and wash thoroughly with a 5-per cent solution of ammonium nitrate. Transfer the paper and precipitate to a platinum crucible, heat very gradually till the paper is dried and charred, gradually ignite until the paper is burned, and finally heat to 1050° C for 15 minutes.

The ignited precipitate will be contaminated with tungstic oxide, if tungsten is present, and with silica, chromium carbides, and titanium phosphate.

In the absence of tungsten and chromium carbides, add 2 ml of  $\text{H}_2\text{SO}_4$  and 5 to 10 ml of HF, and evaporate to dense fumes of sulphur trioxide to eliminate silica. If much chromium is present, particularly if the carbon is over 0.08 per cent, transfer the precipitate to a small porcelain or platinum dish, a crucible, or a beaker, add 5 ml of nitric acid and 5 ml of perchloric acid, and evaporate to fumes. Cool somewhat, add a few drops of hydrofluoric acid, and evaporate to dense fumes of perchloric acid.

After volatilizing the silica, transfer the solution to a 150-ml beaker, rinsing the crucible or dish with 5 ml of HCl and water. Dilute to 75 ml with warm water, add 1 or 2 ml of the 30-per cent hydrogen peroxide, and reprecipitate the zirconium by adding 25 ml of water containing 3 g of diammonium phosphate, stirring vigorously and allowing to stand for at least 30 minutes at 70° C. Filter with the aid of paper pulp, wash 15 times with 2-per cent HCl solution. Ignite carefully and weigh as  $\text{ZrP}_2\text{O}_7$ , 34.39 per cent of which is zirconium.

To test the ignited precipitate for titanium in an exact analysis, fuse the ignited precipitate with a little  $\text{K}_2\text{S}_2\text{O}_7$ , dissolve in 10-per cent  $\text{H}_2\text{SO}_4$ , and add  $\text{H}_2\text{O}_2$  as in the color method for titanium.

In the presence of tungsten, and provided it has not been previously removed, add to the crucible pure sodium carbonate equal to about 10 times the weight of the ignited precipitate, mix, and fuse until the melt is clear. Leach the fused mass with hot water, and cool the solution to room temperature. Filter through a tight paper, containing a little ashless paper pulp, and wash the sodium titanate and zirconate 15 to 20 times with a 2-per cent solution of ammonium nitrate to remove sodium salts, especially of tungstic acid. Ignite the paper and precipitate gradually to a dull red heat until the paper is burned completely. Fuse the residue with 2 or 3 g of potassium pyrosulphate, dissolve the melt in dilute sulphuric acid (5-per cent), and determine

titanium by color (see page 192), using a titanium sulphate standard. If desired, calculate the total weight of the titanium and multiply by 3.16 to find the weight of  $Ti_2P_2O_9$ . Now add diammonium phosphate and reprecipitate the zirconium as before. Ignite the precipitate carefully, add 5 ml of HF, 1 drop of  $H_2SO_4$ , evaporate, ignite, and weigh as  $ZrP_2O_7$ , which multiply by 34.39 and divide by the weight of sample taken to find the per cent zirconium.

### Direct Phosphate Method in Reduced Solution <sup>3</sup>

For zirconium in carbon and low-alloy steels in the absence of columbium, tantalum, and tin.

Transfer 3 g of the sample to a 400-ml beaker, dissolve with 40 ml of HCl (sp. gr. 1.13), and oxidize with 10 ml of nitric acid. Add 20 ml of  $H_2SO_4$  and evaporate till copious fumes of sulphuric acid are evolved. Cool, add 200 ml of water and 5 ml of  $H_2SO_4$ , and warm till salts have dissolved. Boil 2 minutes, filter, and wash with dilute  $H_2SO_4$  (3-per cent). Ignite the residue, cool, add a few drops of dilute  $H_2SO_4$  (1:1), and volatilize the silica by evaporating slowly with HF. Calculate the per cent silica from the loss in weight.

Fuse the residue with sodium bisulphate, in the absence of tungsten, and add the melt to the filtrate. In the presence of tungsten, fuse with sodium carbonate, take up in water, acidify, add a considerable excess of ammonia, filter, burn the paper, and add the residue to the filtrate.

Almost neutralize the filtrate with ammonia, dilute to 400 ml, boil, and add 10 ml of ammonium bisulphite while stirring briskly. Boil gently for 5 minutes, neutralize with ammonia, and add 5 ml of sulphuric acid, holding the total free acid to less than 2 per cent by volume. Heat to boiling, stir in 5 ml more of the ammonium bisulphite, boil 1 minute, and add 15 ml of a 10-per cent solution of sodium or ammonium phosphate for each 0.5 per cent zirconium expected. Stir well and let the mixture stand for at least 4 hours.

Place a little paper pulp in the tip of a close filter, collect the precipitate thereon, and wash it first with dilute sulphuric acid (5-per cent) and then with a 5-per cent solution of ammonium nitrate. Ignite gradually at a low temperature until the paper is charred and finally at a bright red heat. In the absence of titanium, cool in a desiccator and weigh as  $ZrP_2O_7$ , 34.39 per cent of which is zirconium.

In the presence of titanium, fuse the ignited precipitate with a little  $K_2S_2O_7$ , dissolve in dilute sulphuric acid, determine titanium by the color method, and correct the result accordingly.

### Complete Phosphate Method Modified for Application to All Steels Except High-Chromium

**Solution of Sample in Absence of Tungsten.**—Dissolve 5 g of the sample in 60 ml of dilute  $H_2SO_4$  (1:3) and evaporate to fumes of  $H_2SO_4$ . Take up in 100 ml of  $H_2O$ , boiling till salts have dissolved,



stir in a little paper pulp, filter on a close filter, and wash with hot water. Reserve the filtrate and washings, and treat the residue as follows for the elimination of silica.

If the residue is heavy and dark, indicating much copper or carbides, ignite in a porcelain crucible and transfer to a platinum crucible. If the residue is mainly silica, ignite in a platinum crucible. Cool, add 3 ml of  $\text{H}_2\text{SO}_4$  and 3 ml or more of  $\text{HF}$ , and evaporate in a hot air bath to dense fumes of sulphur trioxide. Cool and transfer to the original filtrate.

**Solution of Sample in Presence of Tungsten.**—Treat the sample as in the determination of tungsten. Evaporate the filtrate from tungstic acid and treat with  $\text{HCl}$  to expel  $\text{HNO}_3$ . Dissolve the tungstic acid with ammonia, get the residue into hydrochloric acid solution, fusing with  $\text{K}_2\text{S}_2\text{O}_7$  if necessary, and add to the original filtrate.

**Reduction of Iron and Separation of Copper, etc.**—Dilute the combined filtrates to 250 ml, heat to boiling, and add 5 ml of a 30-per cent solution of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , sodium hyposulphite) to precipitate copper, reduce the iron, etc. Boil 5 minutes, filter, wash with hot water, and discard the precipitate.

To test the residue for titanium and zirconium, ignite the precipitate in porcelain, dissolve with a little nitric acid, fume with  $\text{H}_2\text{SO}_4$ , dilute and pour into dilute ammonia (1:1), filter, wash with dilute ammonia, and ignite in a platinum crucible. Fuse with  $\text{K}_2\text{S}_2\text{O}_7$ , if a residue remains, and add to the main solution.

**Precipitation with Phosphate.**—To the clear filtrate, add 30 ml of  $\text{H}_2\text{SO}_4$  and heat to  $60^\circ \text{C}$ . Add 25 ml of a 20-per cent solution of  $(\text{NH}_4)_2\text{HPO}_4$ , stir vigorously for 5 minutes, and digest for 2 hours. Stir in a little paper pulp, let the insolubles settle, and filter on a tight paper. Wash the beaker, the filter, and the precipitate thoroughly with a 5-per cent solution of ammonium nitrate, transfer to a platinum crucible, ignite at a low temperature until the paper is charred, and then gradually heat to about  $1050^\circ \text{F}$ . Cool and weigh as  $\text{ZrP}_2\text{O}_7$ , in routine work with all steels except those containing columbium, tantalum, or much titanium. Multiply by 34.39 and divide by 5 to find the per cent Zr.

In exact analyses and in the analysis of some complex alloy steels, the precipitate is examined for contaminants. The precipitate may be contaminated with iron, titanium, or tin, and with chromium, columbium, and tantalum, if the fourth is present in large percentages and the last two are present at all. Also, if much zirconium is present, an error may be introduced through the varying composition of the precipitate.

To purify the precipitate from iron and titanium, fuse the ignited precipitate with 2 or 3 g of  $\text{K}_2\text{S}_2\text{O}_7$ , dissolve the melt in 75 ml of 10-per cent  $\text{H}_2\text{SO}_4$ , add 15 ml of 3-per cent  $\text{H}_2\text{O}_2$ , determine the titanium

present by color, if desired, heat to 60° C, add 5 ml of  $\text{H}_2\text{SO}_4$  and 15 ml of 20-per cent  $(\text{NH}_4)_2\text{HPO}_4$ . Stir briskly for several minutes, digest 2 hours at 60° C, filter, and weigh as before.

If titanium is estimated by color, an idea of the iron in the precipitate is obtained.

To remove tin, fuse with 5 g of sodium carbonate. Leach with water, filter, wash with water, ignite, fuse with  $\text{K}_2\text{S}_2\text{O}_7$ , and reprecipitate as before.

To remove columbium and tantalum, fuse in a nickel crucible with 5 g of KOH, instead of  $\text{Na}_2\text{CO}_3$ .

### Standard Procedures Based Upon Separation of Zirconium with Cupferron

#### Cupferron Phosphate Method, Absence of Columbium, Tantalum, and Tin

**Cupferron Solution Required.**—Prepare as needed by dissolving 2 g in 35 ml of water.

**Weight of Sample.**—For carbon steel, ingot iron, wrought iron, and alloy steels, to which zirconium has not been added, use 5 g of sample.

For zirconium steels, use 2 g or 3 g according to the probable amount of zirconium present.

Ferrozirconium is powdered, 1 g transferred to a platinum crucible or dish, treated with 5 ml of  $\text{H}_2\text{SO}_4$  and 15 ml of hydrofluoric acid, evaporated in an air bath, fumed, taken up in hydrochloric acid, diluted to 200 ml, and 50 ml, corresponding to 0.25 g, is taken for analysis, and diluted to 150 ml. This initial treatment is necessary on account of the high percentage of silicon present.

**Procedure.**—*Solution of Sample and Separation with Cupferron.* Transfer the correct weight of sample to a 250-ml beaker, add 50 ml of dilute HCl (1:4), plus 20 ml for each gram of cuttings, and heat gently till the metal is dissolved. Cool to 20° C, dilute to 150 ml, add cupferron solution with constant stirring until the precipitate assumes a reddish brown color, stir in some paper pulp, and filter on an 11-cm paper. Wash 15 times with dilute HCl (1:9), transfer paper and contents to a platinum crucible, ignite gradually to 550° C, and fuse with  $\text{K}_2\text{S}_2\text{O}_7$ . Dissolve the melt in 100 ml of dilute  $\text{H}_2\text{SO}_4$  (1:9), filter, and wash with 50 ml of the same acid.

**Precipitation as Phosphate.**—Stir in 2-3 ml of 30-per cent  $\text{H}_2\text{O}_2$  and 3 g of  $(\text{NH}_4)_2\text{HPO}_4$  dissolved in 20-25 ml water, then heat to 60° C while stirring vigorously, and let the beaker stand for at least 1 hour; and for 8 to 12 hours, if zirconium is low, adding 1 or 2 drops of  $\text{H}_2\text{O}_2$  from time to time. Filter with the aid of paper pulp, and wash 8 to 10 times with a cold 5-per cent solution of  $\text{NH}_4\text{NO}_3$ . Transfer the paper and contents to a weighed platinum crucible, char the paper

slowly, burn the carbon off, and gradually ignite to  $1050^{\circ}\text{C}$  for 10 or 15 minutes. Cool and weigh as impure  $\text{ZrP}_2\text{O}_7$ , unless titanium and interfering elements are known to be absent.

To test for titanium, fuse with 3 or 4 g of  $\text{K}_2\text{S}_2\text{O}_7$ , dissolve in 40 ml dilute  $\text{H}_2\text{SO}_4$  (1:9), add 5 ml of 3-per cent  $\text{H}_2\text{O}_2$ , and estimate titanium by color, using standard titanium sulphate solution added to a blank test prepared in the same way. Calculate Ti to  $\text{TiP}_2\text{O}_7$  and subtract from the weight of  $\text{ZrP}_2\text{O}_7$ .

Multiply the corrected weight of  $\text{ZrP}_2\text{O}_7$  by 34.39 and by 100 and divide by the weight of sample used to find the per cent zirconium.

#### Methods Depending upon Separation of Zirconium with Phenylarsonic Acid and Weighing as Zirconium Oxide

The following methods provide for the accurate determination of zirconium in all steels except those containing much columbium or tantalum, when the final result cannot be taken as representing only zirconium without examination of the  $\text{ZrO}_2$  to establish its purity. Columbium up to 0.30 per cent does not interfere, and larger percentages may not, if care is taken to provide a sufficient excess of  $\text{H}_2\text{O}_2$  in the final precipitation.

Also, by proper modifications, the methods have been adapted for the determination of silicon and zirconium; of silicon, zirconium, and columbium; or of silicon, tungsten, and zirconium on the same sample.

#### Special Solution Required

Prepare a saturated water solution of phenylarsonic acid, filter, and dilute to give a 2-per cent or a 2.5-per cent solution. For the precipitation of 1 mg of zirconium at least 5 mg of phenylarsonic acid are required.

#### Procedure Involving a Preliminary Separation With Ether

**Solution of Sample.**—*Presence of Tungsten.*—Dissolve 2 g in 50 ml of dilute  $\text{HCl}$  (sp. gr. 1.10), and add  $\text{HNO}_3$  (sp. gr. 1.42), dropwise, to oxidize the iron and tungsten, finally adding an excess of about 5 ml. Boil the solution until the tungstic acid is a bright yellow in color, dilute to 150 ml, and filter. If it is desired to determine tungsten, proceed as usual, fuse the  $\text{WO}_3$  with  $\text{Na}_2\text{CO}_3$ , take up in water, filter and ignite, and fuse any residue with  $\text{K}_2\text{S}_2\text{O}_7$ . Dissolve in acid and add to the acid solution after extraction with ether. If tungsten is not desired, dissolve the tungstic acid with ammonia, dissolve any residue remaining with  $\text{HCl}$ , and add to the original filtrate.

To expel nitric acid, evaporate the filtrate almost to dryness, add  $\text{HCl}$ , evaporate again, and take up in 10 ml of dilute  $\text{HCl}$  (sp. gr. 1.13); and proceed with the ether separation as described under *Chemical Separations*. If a residue remains, dilute, filter it off, wash and add

it to the residue from the tungsten, evaporate the filtrate a third time, and take up with HCl.

*Absence of Tungsten.*—Dissolve 5 g in 60 ml of dilute HCl (sp. gr. 1.10) and add  $\text{HNO}_3$ , dropwise, until the iron is just oxidized. Evaporate just to dryness, take up in 25 ml of HCl (sp. gr. 1.19), warming but not boiling, and proceed with the ether extraction as described under *Chemical Separations*, but washing the ether once with 25 ml of the acid. If an insoluble residue remains after evaporating, dilute, filter it off, fuse with  $\text{NaHSO}_4$ , take up in dilute  $\text{H}_2\text{SO}_4$ , and add to the acid solution from the ether extract. Evaporate the filtrate and washings again to dryness, and continue as directed above.

**Precipitation of Zirconium.**—Heat the acid solution on a bath to the expulsion of the ether, dilute to 400 ml, and add HCl if necessary to adjust the acidity so that the solution contains 8 to 10 per cent of this acid. Add 50 ml of a 3-per cent hydrogen peroxide or 5 ml of 30-per cent, and stir in sufficient of the phenylarsonic acid solution to precipitate all the zirconium and give a considerable excess. Heat the solution to boiling, and boil at least 5 minutes. Filter, wash thoroughly with dilute hydrochloric acid (1:99), transfer to a new clean porcelain crucible, burn the paper, and ignite under a hood. Brush the residue into a weighed platinum crucible, add 2 or 3 drops of  $\text{H}_2\text{SO}_4$ , 2 or 3 ml of HF, evaporate, and ignite gradually, finally at  $1000^\circ\text{C}$  or above for 15 to 20 minutes. Weigh as  $\text{ZrO}_2$ . Multiply by 74.03 and divide by 5 to find the per cent zirconium.

#### Procedure Involving a Double Precipitation With Phenylarsonic Acid Without a Previous Separation

**Solution of Sample.**—Transfer 5 g of the sample to a 400-ml beaker and dissolve, preferably in dilute  $\text{H}_2\text{SO}_4$ , or in HCl or HCl and  $\text{HNO}_3$ , when tungsten is present, which must be separated and treated as directed in the preceding method. If HCl and  $\text{HNO}_3$  are used, add  $\text{H}_2\text{SO}_4$  and evaporate to fumes, using 10 ml for this purpose. Cool, add 50 ml of water, heat gently, and stir to dissolve sulphate. If a residue remains, filter, and wash with hot water, collecting filtrate and washings in a 600-ml beaker. Ignite and fuse the residue with 10 times its weight of sodium carbonate, leach with hot water, filter, wash with water, and discard the filtrate. Ignite and fuse this residue with a little  $\text{K}_2\text{S}_2\text{O}_7$  and dissolve in the original filtrate.

**Precipitation of Zirconium.**—To the combined filtrates, add 20 ml HCl and dilute to 200 ml. Add 5 ml of 30-per cent  $\text{H}_2\text{O}_2$  and heat to boiling. To precipitate zirconium add 10 ml of a 2-per cent aqueous solution of phenylarsonic acid (sufficient for 0.05 g Zr) and boil for 1 minute. Filter hot and wash with hot dilute HCl (1-per cent). Transfer the paper and precipitate to the 600-ml beaker, add 40 ml of dilute HCl (1:1), cover, and digest on a hot plate until the paper is disin-

tegrated. Dilute to 200 ml with hot water, heat to boiling, add 5 ml of the phenylarsonic acid, and boil 1 minute. Filter, wash as before, heat slowly in a weighed porcelain crucible, until the paper is charred, and ignite to constant weight at 1100° C. Cool and weigh as  $\text{ZrO}_2$ . Multiply by 74.03 and divide by 5 to find the per cent zirconium in the sample.

**Procedure Using Double Precipitation With Phenylarsonic Acid for Stainless and Other High-Alloy Steels Containing No Tungsten**

Transfer 5 g of the sample to a 400-ml beaker, add 60 ml of dilute HCl (1:1) and 60 ml of water, and heat to 60° C until the metal dissolves. Start a blank test in the same way. Add 8 ml of perchloric acid (70-per cent) and evaporate to fumes. Fume 2 or 3 minutes at lowest temperature possible, cool somewhat, add 20 ml of HCl, and agitate till salts dissolve. Add 10 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1), then, carefully, 5 ml of 3-per cent  $\text{H}_2\text{O}_2$ , and allow the mixture to simmer a few minutes. Dilute with hot water to 500 ml, stir, and add 6 ml of phenylarsonic acid solution. Boil 1.5 minutes, add paper pulp, stir, rinse the wall of the beaker with warm dilute HCl (1-per cent), and let the beaker stand a few minutes. Filter through a close paper and wash with dilute HCl (1-per cent). Set the filtrate aside, and hold the original beaker for the second precipitation.

Transfer the paper and contents to a porcelain crucible, dry on a hot plate, and ignite slowly under a good hood to burn paper and drive off arsenic. Cool, add 2 g of  $\text{KHSO}_4$ , cover, and fuse over a low flame, raising the temperature to a cherry red after the first violent action is over. Cool to a cake, add 2 rice-size crystals of  $\text{KNO}_3$  and about 1 g of  $\text{KHSO}_4$ . Then cover the crucible and heat till the salt melts and oxides of nitrogen are expelled, and heat over the full flame of a Meker burner for 5 to 8 minutes. Cool, place the crucible in the original beaker, add 20 ml HCl, 100 ml  $\text{H}_2\text{O}$ , and 5 ml of  $\text{H}_2\text{O}_2$  (30-per cent); and heat to 60° C until the melt dissolves. Remove and rinse the crucible and cover, and raise the temperature of the solution to 100° C for 15 to 20 minutes or until all but silica has dissolved. Add 5 ml of 3-per cent  $\text{H}_2\text{O}_2$  and dilute to 500 ml with hot water. Add 6 ml of phenylarsonic acid solution, boil for 1.5 minutes, filter, and wash with 1-per cent HCl.

Transfer the filter paper and contents to the crucible, dry, and ignite as before. When the arsenic that sublimes on the wall of the crucible has all been driven off, ignite to 1000° C or higher for 5 to 10 minutes. Cool, transfer the residue to a weighed platinum crucible, moisten it with dilute  $\text{H}_2\text{SO}_4$  (1:3), and add 2 to 3 ml of HF. Evaporate under a hot plate or in an air bath to prevent zirconium fluoride from creeping over the edge of the crucible, and finally ignite to about

1050° C. Cool, weigh as  $\text{ZrO}_2$ , subtract the blank, multiply by 74.03, and divide by 5 to find the per cent zirconium in the sample.

If much columbium, tantalum, or tin is present, examine the  $\text{ZrO}_2$  for these elements as directed for the complete phosphate method.

### Procedure Adapting the Phenylarsonic Acid Method to the Determination of Silicon, Columbium and Zirconium

The following procedures, developed and used by Duquesne Works Laboratory of Carnegie-Illinois Steel Corporation, are designed for the determination of silicon and zirconium in any steel. They provide for the removal of interfering elements and others that may contaminate the final precipitate.

#### Special Reagents Required

**Phenylarsonic Acid.**—Two-per cent solution, filtered clear.

**"Red Acid" Mixture.**—Mix equal parts of  $\text{HCl}$  and  $\text{HNO}_3$  and allow the mixture to stand several hours until it becomes a deep red in color.

#### Procedure

**I. Columbium and Tungsten Absent.**—*Solution of the Sample.* Transfer 2.336 g of the sample to a 400-ml beaker, and dissolve the cuttings by treating in either of two ways, as follows:

(1) Cover the beaker, add 30 ml of the "red acid" mixture, and heat gently if necessary to hasten the action of the acid on the steel. When the cuttings have been dissolved, boil the solution down to a low volume to insure complete decomposition of any carbides.

(2) Cover the beaker, add 15 ml of water and 45 ml of  $\text{HCl}$ , and heat gently until the cuttings have dissolved. To decompose any dark or black residue remaining insoluble in the  $\text{HCl}$ , treat the mixture with dilute nitric acid (sp. gr. 1.20) as follows: Measure 15 ml of the acid in a graduate, and add 5 or 6 drops to the beaker. Wait 1 or 2 minutes before adding more of the acid, and repeat the additions in this manner until an effervescence occurs on adding the acid. Then add the rest of the acid and boil down to a small volume.

*Separation and Determination of Silicon.*—Add 35 ml of perchloric acid (55-per cent) to the beaker and evaporate to fumes. Heat for 10 minutes after the perchloric acid is condensing on the wall of the beaker, then cool rapidly in running water and add 150 ml of water. Stir to dissolve salts, and filter immediately through a paper of close texture, collecting the filtrate in a 600-ml beaker for treatment as directed below for the precipitation of zirconium. Wash the filter and contents 5 or 6 times with dilute  $\text{HCl}$  (5-per cent), and treat it as directed below for the volatilization of the  $\text{SiO}_2$  and the recovery of any of the zirconium with which it may be contaminated.

Transfer the filter and contents to a 30-ml platinum crucible and gradually ignite to  $950^{\circ}\text{C}$  for 15 minutes. Cool and weigh the crucible. Then moisten its contents with a few drops of dilute  $\text{H}_2\text{SO}_4$  (1:1), add 5 to 7 ml of  $\text{HF}$  (48-per cent), and evaporate to apparent dryness under a hot plate or in an air bath. To drive off  $\text{H}_2\text{SO}_4$  and avoid loss from spitting, heat the crucible gradually from the top downward until the last visible trace of  $\text{H}_2\text{SO}_4$  has been expelled, and ignite as before. Cool, weigh, and treat the residue as directed below. Subtract this weight from the previous one. Multiply the difference by 20 to find the per cent silicon in the sample.

*First Precipitation of Zirconium.*—To the filtrate from the silica, add 10 ml of  $\text{HCl}$  and stir in  $\text{H}_2\text{O}_2$  (3-per cent) until the chromium is reduced and there is an excess of about 10 ml. Add 20 ml of a 2-per cent solution of phenylarsonic acid, heat to boiling, and boil 1 minute. Let the beaker stand until the white flocculent precipitate of zirconyl phenylarsonate has settled somewhat. Filter the solution and wash the beaker and filter with 5-per cent  $\text{HCl}$  containing 5 ml of  $\text{H}_2\text{O}_2$  (3-per cent) per 100 ml of acid solution. Discard the filtrate and transfer the filter paper and contents to the beaker in which the precipitation was made. Add 30 ml of dilute  $\text{HCl}$  (1:1), macerate the paper, heat to dissolve impurities from the insoluble zirconyl phenylarsonate, and add the solution containing the small portion of the zirconium recovered as follows:

*Recovery of Zirconium from Silicon Residue.*—To the crucible containing the residue from the volatilized silica, add 2 to 3 g of  $\text{KHSO}_4$  and fuse at a low temperature until the melt is clear. Grasp the crucible with tongs and tilt it with a revolving motion as it cools so that the melt will solidify in a thin layer upon the wall. Add 10 ml of dilute  $\text{HCl}$  (1:1), heat gently to dissolve the cake, and transfer the solution to the beaker containing the main portion of the zirconium.

*Treatment to Determine Total Zirconium.*—Add to the beaker, which now contains all of the zirconium, water to make a volume of 200 ml. While stirring, add 10 ml of  $\text{H}_2\text{O}_2$  (3-per cent) and 10 ml of phenylarsonic acid (2-per cent) and boil 1 minute. Let the precipitate settle somewhat, then filter and wash with dilute  $\text{HCl}$  (5-per cent). Transfer the filter and contents to a weighed platinum crucible, dry, and char the paper at a low temperature. Burn off the paper and ignite gradually to a temperature of  $1000^{\circ}$  to  $1050^{\circ}\text{C}$  for 1 hour. Cool, weigh, and reignite to constant weight. To find the per cent zirconium in the sample, multiply the final weight of the  $\text{ZrO}_2$  by 31.69.

**II. Columbium Present, Tungsten Absent.**—Proceed as directed under I for the *Solution of the Sample and Determination of Silicon*, and treat the filtrate from the silica for the recovery of a part of the columbium as follows:

*First Precipitation of Columbium.*—Add to the filtrate from the silica 10 ml of  $\text{HCl}$  and boil the solution 10 minutes to precipitate the

columbium. Filter the solution and wash the filter and contents with dilute HCl (5-per cent). Reserve both the filtrate and the precipitate for treatment as directed below:

*Fusion of the Residues.*—Add the paper and contents to the crucible containing the residue left after volatilizing the silica, thus gathering all of the columbium and a part of the zirconium. Dry and burn off the paper gradually. Add 2 to 3 g of potassium bisulphate and fuse as directed above for the recovery of zirconium. Add 10 ml of dilute HCl (1:1) to the crucible and digest to disintegrate the cake. Transfer the contents of the crucible to a 400-ml beaker and treat for the separation and determination of columbium as directed below.

*Separation and Determination of Columbium.*—Add water to the beaker to make the total volume 150 ml and boil for 10 minutes to precipitate the columbium. Add paper pulp, filter, and wash with a 5-per cent solution of HCl. Reserve the filtrate for recovery of zirconium. Transfer the paper and contents to a weighed platinum crucible, gradually ignite to constant weight at  $1000^{\circ}\text{C}$ , and weigh as  $\text{Cb}_2\text{O}_5$ . Multiply the weight of the  $\text{Cb}_2\text{O}_5$  by 29.96 to obtain the per cent columbium in the sample.

*Recovery and Determination of Zirconium.*—Treat the filtrate from the first precipitation of columbium for the precipitation of zirconium with phenylarsonic acid as directed under *First Precipitation of Zirconium* in the absence of columbium.

Add the filtrate obtained in the separation and determination of columbium as directed above to the beaker containing the zirconyl phenylarsonate digested in HCl solution. Add water to make a total volume of 200 ml, and complete the determination as directed for zirconium in the absence of columbium under the heading *Treatment to Determine Total Zirconium*.

**III. Columbium and Tungsten Present.**—*Recovery of Zirconium, Columbium, and Tungsten.*—Dissolve the sample (2.336 g) with HCl and proceed as directed for silicon in the absence of tungsten and columbium, which treatment will leave much of the tungsten and some of the zirconium with the silica. After filtering off the silica, ignite, volatilize  $\text{SiO}_2$ , reserve the residue, and treat the filtrate as follows: Add 10 ml of HCl to the filtrate, boil for 10 minutes, and filter, if any precipitate appears, as it may be columbium or tungsten or both. Wash this precipitate with dilute HCl (5-per cent) and reserve it for treatment as directed below for the separation of zirconium. To this second filtrate, add 5 ml of cinchonine solution (125 g cinchonine in 500 ml HCl + 500 ml  $\text{H}_2\text{O}$ ), boil, and let the beaker stand 12 hours or longer to complete the precipitation of the tungsten. Filter, wash with 5-per cent HCl, and reserve both the paper and the filtrate for treatment as directed below.



*First Precipitation of Zirconium.*—Treat the filtrate for the precipitation of the zirconium as zirconyl phenylarsonate as directed under this heading in the absence of columbium and tungsten. Reserve the acid cleansed zirconyl phenylarsonate for use as directed later.

*Separation and Recovery of Zirconium from the Residues and Estimation of Tungsten in the Absence of Columbium.*—Transfer the 2 filter papers containing the columbium and tungsten to the crucible containing the residue from the silica and ignite slowly to a temperature sufficiently high to burn the papers completely. Cool and weigh the crucible and contents which consist of the oxides of Fe, Zr, Cb, W, and P. Add 5 g of  $\text{Na}_2\text{CO}_3$  and fuse completely. Insert a platinum rod into the melt with the crucible tilted to one side and allow the melt to solidify. Grasp the rod with one hand and with a pair of tongs hold the crucible over a Meker burner flame until the cake on the end of the rod can be lifted out. Transfer the latter to a 400-ml beaker containing 100 ml of water and scrub the crucible thoroughly with hot water, adding the rinsings to the crucible. Reserve the crucible for use later. Boil the contents of the beaker for 5 to 7 minutes and filter through a 9-cm paper of close texture into an 800-ml beaker. Wash the beaker twice and the paper thoroughly with a 2-per cent solution of sodium carbonate, and reserve the filtrate, which contains columbium, tungsten, and phosphorus.

Transfer the filter paper, which contains the zirconium as sodium zirconate, to the beaker in which the fusion was digested. Wash the crucible in which the fusion was made with 15 ml of dilute HCl (1:1) and add these washings to the beaker. Add an additional 15 ml of the acid and heat gently for 8 to 10 minutes. Add 170 ml of water, 2 or 3 drops of methyl red indicator solution, and ammonia until the color of the solution just changes to yellow. Boil 1 minute, adding more of the ammonia if necessary to keep the color yellow. Filter and wash with hot water. Ignite in the same platinum crucible used previously, cool, and weigh as the oxides of Fe, Zr, and P. Subtract this weight from the previous weight and designate the difference as  $\text{CB}_2\text{O}_5 + \text{WO}_3$ . In the absence of columbium, calculate the difference to per cent tungsten, using factors given under *Determination of Tungsten*.

*Recovery and Determination of Zirconium.*—Fuse the mixed oxides of Fe, Zr, and P obtained as directed above with 2 to 3 g of sodium or potassium bisulphate. Cool and dissolve the melt in 10 ml of dilute HCl (1:1) and add the solution to the zirconyl phenylarsonate obtained as directed under *First Precipitation of Zirconium*. Precipitate the zirconium in solution and determine zirconium as directed under *Treatment to Determine Total Zirconium*.

*Separation and Determination of Columbium and Tungsten.*—Add to the carbonate solution obtained in separating the zirconium 15 ml of HCl and boil 10 minutes. Digest until the precipitate settles and

filter through a small close paper. Wash the beaker and filter 3 or 4 times with a 5-per cent solution of HCl, and then with water till free of acid. Spread the paper out on the bottom of the beaker in which the precipitation was made, add the fresh solution of ammonium salicylate prepared as directed below, and digest for 2 to 3 hours. Filter and wash 4 times with hot water. Ignite the filter and precipitate in a weighed platinum crucible, cool, and weigh as  $\text{Cb}_2\text{O}_5$ . Multiply this weight in grams by 29.92 to find the per cent columbium in the sample.

To prepare the ammonium salicylate solution, add 13 g of salicylic acid to 280 ml of water. Then add 2 or 3 drops of brom-cresol purple indicator solution, and stir in ammonia slowly until the color of the solution just changes to purple. Filter, add exactly 2 g of salicylic acid, and dilute to 300 to 350 ml.

*Estimation of Tungsten.*—From the weight of  $\text{Cb}_2\text{O}_5 + \text{WO}_3$  (columbic + tungstic oxides), deduct the weight of the  $\text{Cb}_2\text{O}_3$  and designate the difference as  $\text{WO}_3$ , 79.31 per cent of which is W. For the weight of sample specified herein, multiply the difference by 33.95 to obtain the per cent tungsten in the sample.

Note. If the per cent tungsten is much higher than the per cent of columbium, the separation with acid ammonium salicylate may not be complete.

#### Text References

1. Rice, A. C., Fogg, H. C., and James, C., *J. Am. Chem. Soc.*, **48**, 895 (1926).  
Arnold, F. W., Jr., and Chandlee, G. C., *J. Am. Chem. Soc.*, **57**, 8 (1935).  
Knapper, J. S., Craig, K. A., and Chandlee, G. C., *J. Am. Chem. Soc.*, **55**, 3945 (1933).
2. *Arch. Eisenhütten W.* **7**, 133 (1935) Klinger and Schliessman.
3. Johnson, C. M., "Chemical Analysis of Special Steels," New York, John Wiley and Sons, Inc., 1930.

#### General References

- Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel," New York, John Wiley and Sons, Inc., 1931.
- "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Alloy Steels," Second Edition, 1921.
- Klinger, P., "The Determination of Zirconium by the Aid of Phenylarsonic Acid," *Technical Communications, Krupp*. Vol. 3, Part 1, March, 1935.

# Determination of Columbium and Tantalum

Like titanium, columbium, also known as niobium, is added to stainless and heat-resistant steels to make them softer and more ductile, and to overcome intergranular corrosion. The use of tantalum is still in the experimental stage. In analytical work on these steels, these three elements must also be considered in relation to selenium which is added to improve machining properties, and possibly with zirconium, which usually carries a little hafnium with it. Among elements occurring in steel, columbium, titanium, tantalum, and zirconium are to be classed among the rarer elements, and treatments with ordinary reagents generally leave them closely associated. Consequently, their isolation and determination have presented a difficult problem not yet completely and wholly satisfactorily solved.

## Methods Available

The umpire method recommended by Lundell, Hoffman, and Bright provides for the determination of columbium, tantalum, titanium, and zirconium on the same sample,<sup>1</sup> and is recommended as a means of checking results by other methods. Another method that has been found satisfactory is that proposed by T. R. Cunningham<sup>3</sup> and this method, with permissible modifications introduced is given as the second method recommended as a standard routine procedure for columbium and tantalum in stainless steels. In both methods, the group of elements mentioned above are separated and weighed together as the mixed oxides,  $\text{Cb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ , plus  $\text{TiO}_2$ , and  $\text{ZrO}_2$ , as impurities, following which step the titanium is determined by color, columbium is reduced with zinc in a Jones reductor, collected under ferric sulphate and titrated indirectly with  $\text{KMnO}_4$ , tantalum being found by difference. No provision is made in the method for the separation of zirconium, and it employs a fusion, which, if made in platinum, will throw more error on the tantalum. In a third method,<sup>2</sup> the columbium is separated and determined along with the silicon by fuming with perchloric acid, diluting, boiling, filtering, and volatilizing the silica with  $\text{HF}$ . Our researches indicate some silica is held in solution by this procedure, that the residue may be contaminated with iron, aluminum, tantalum, titanium, tin, zirconium, etc., and that the method is subject to other objections as well. Therefore, the residue must be purified by fusing with  $\text{NaHSO}_4$ , acidifying and reprecipitating.

The following methods, some steps of which have been adapted from the sources named above, represent those in use at present for the

determination of these elements except the method for columbium already given under *Methods for Zirconium*. In general, methods adapted to routine work, though of limited application, are given first, and these are followed by the more tedious methods, which may be applied for various purposes in which time is not important.

**Procedure for the Determination of Silicon and Columbium  
in Stainless and Other Alloy Steels Containing No  
Tungsten or Tantalum: Gravimetric Method**

**Application and Accuracy of the Method**

The following method has been found to give satisfactory results for both silicon and columbium when applied to steels of the class indicated by the heading. It has been checked by comparing results it gives with those obtained by more tedious methods, and also by analysis of a columbium-free stainless steel standard to which known amounts of columbium in solution have been added. Titanium and zirconium do not interfere, though much titanium tends to prevent the hydrolysis of the columbium by which it is precipitated and thus separated from other elements. Tantalum, if present, will accompany columbium and be found in the final precipitate. Tungsten, even when present in small quantities, is partly precipitated with the columbium, and the method must be modified as described under zirconium with columbium and tungsten present.

**Procedure**

**Solution of the Sample and Separation of Silicon.**—Transfer 2.336 g of the sample to a 400-ml beaker and cover with a watch glass. Add 20 ml of HCl and heat gently till the cuttings have dissolved. Oxidize the solution by adding 10 ml of HNO<sub>3</sub>, dropwise, and boil to a small volume. Add 35 ml of 55-per cent HClO<sub>4</sub> and continue the evaporation under cover to fumes. Starting from the time when the perchloric acid is condensing and running down the inner wall of the beaker, continue the heating for 10 minutes to completely oxidize the chromium and dehydrate the silicic acid. Grasping the beaker with a pair of tongs, cool it rapidly by dipping in and out of running water. Add 150 ml of cold water, stir to hasten the solution of salts, and filter the solution immediately through a close paper. Clean the beaker and wash the filter rapidly with a 2-per cent solution of HCl. Avoid delay in filtering, also heating the solution, or the use of hot water and hot acid, as these are factors that increase the solubility of the silica. Reserve both the filtrate and the filter for treatment as directed below:

**Determination of Silicon and Recovery of Columbium.**—Transfer the filter paper and contents to a clean 30-ml platinum crucible, and ignite at a low temperature until the paper has burned completely, then at 1050° to 1100° C for at least 15 minutes. Cool and weigh

the crucible and contents. Add a few drops of dilute  $\text{H}_2\text{SO}_4$  (1:1) and 5 to 7 ml of HF (48-per cent). Evaporate to apparent dryness under a hot plate or in an air bath to avoid spitting. Heat gradually till fumes of sulphuric acid cease to be evolved, and ignite gradually to  $1000^\circ\text{C}$ . Cool and weigh the crucible and contents, and reserve for the ignition of the columbium precipitate, which is recovered from the filtrate as directed below. Subtract the second weight from the first and multiply the difference by 20 to find the per cent silicon in the sample.

**Recovery and Determination of Columbium.**—Boil the filtrate from the silica 10 minutes to precipitate the columbium by hydrolysis. Set a filter paper and fill its tip with paper pulp. Filter the solution through the pulp and wash the beaker and filter thoroughly with dilute HCl (2-per cent), discarding the filtrate. Add the filter and contents to the crucible containing the residue from volatilization of the  $\text{SiO}_2$  and ignite slowly and carefully till the paper is completely burned. Cool the crucible, add 2 to 3 g of  $\text{KHSO}_4$ , and gradually heat the crucible over a burner until the salt has fused. Continue the fusion until the residue from the ignition dissolves. Grasp the crucible with the tongs and rotate while it cools so that the melt solidifies mainly on the inner wall. When the crucible and the fusion have cooled below  $100^\circ\text{C}$ , add 15 ml of dilute HCl (1:1) and heat gently until the fusion dissolves, giving a turbid solution. Transfer the solution to a 400-ml beaker and dilute to 150 ml. Boil 10 minutes to precipitate the columbium which appears as a white flocculent precipitate imparting a milky appearance to the solution. Filter the solution through paper pulp as directed for the first precipitation above and wash the beaker and the filter thoroughly with a 2-per cent solution of HCl. Ignite gradually to  $1000^\circ\text{C}$  to  $1050^\circ\text{C}$  for at least 15 minutes, and multiply the weight of the  $\text{Cb}_2\text{O}_5$  by 29.96 to find the per cent Cb in the sample.

**Procedure for the Determination of Columbium and Tantalum in Stainless and Heat-Resistant Steels in Absence of Tungsten or Much Titanium: Gravimetric-Volumetric Method**

**Applications and Accuracy of the Method**

As mentioned in the introduction under *Methods Available*, the columbium and tantalum are first separated together as the mixed oxides  $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$  and the  $\text{Cb}_2\text{O}_5$  is subsequently reduced and determined volumetrically, preferably, or gravimetrically, if desired. In the volumetric method, the oxide is converted to columbic sulphate,  $\text{Cb}_2(\text{SO}_4)_5$ , reduced in a Jones reductor to columbous sulphate,  $\text{Cb}_2(\text{SO}_4)_3$ , and collected under a solution of ferric sulphate with which the  $\text{Cb}_2(\text{SO}_4)_3$  reacts to form  $\text{Cb}_2(\text{SO}_4)_5$  and a corresponding amount of ferrous sulphate, which is titrated with a standard solution of  $\text{KMnO}_4$ . Complete reduction of columbic sulphate is difficult, but

if the process is carefully carried out as directed, the error is insignificant for the percentage of columbium usually found in steels. In the gravimetric method the pure mixed oxides are weighed, heated to 1050° C in an atmosphere of dry hydrogen, cooled in the same gas, and weighed. The loss in weight represents Cb, as the  $\text{Cb}_2\text{O}_5$  is reduced to  $\text{Cb}_2\text{O}_4$  and  $\text{Ta}_2\text{O}_5$  remains unaffected. For steels containing tungsten or much titanium, the method requires some modification, as the latter is said to hinder the hydrolysis of the columbium, and tungsten, even when present in proportions much smaller than the columbium, is largely included with the columbium in the precipitate.

### Special Solutions Required

**Succinic Acid.**—Dissolve 5 g in 100 ml of water.

**Sulphurous Acid,  $\text{H}_2\text{SO}_3$ .**—Saturate water with  $\text{SO}_2$ , formed in a suitable generator by treating sodium sulphite with dilute  $\text{H}_2\text{SO}_4$ . Use while fresh.

**Ferric Sulphate-Phosphoric Acid Mixture.**—Add 100 g of ferric sulphate to about 500 ml of water, containing 20 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1), mix, add 150 ml of orthophosphoric acid (sp. gr. 1.72), and dilute to 1 liter.

**Standard Solution of Potassium Permanganate, 0.05 N.**—Dissolve 1.6 g of  $\text{KMnO}_4$  in 1000 ml of water. Age for 1 week, filter through purified asbestos, and standardize against National Bureau of Standards sodium oxalate using the standard procedure recommended by the Bureau. One ml of a 0.05 N solution is equivalent to 0.002323 g Cb or 0.003323 g  $\text{Cb}_2\text{O}_5$ .

### Special Apparatus: Jones Reductor

Select 20-mesh zinc with a very low content of iron and amalgamate it thoroughly by transferring 800 g to a 1000-ml flask, adding 400 ml of a 2.5-per cent solution of mercuric chloride, and agitating vigorously for 2 minutes. Decant the liquid, and wash twice by decantation with water.

Prepare a Jones reductor tube having a column some 36 inches long. Fill the tube with warm dilute  $\text{H}_2\text{SO}_4$  (2.5-per cent), open the stopcock, and add the amalgamated zinc as the acid flows out to a depth of 30 inches. Close the stopcock, heat the acid almost to boiling, and add it as the cold acid is allowed to flow out. Close the stopcock just before the acid reaches the top surface of the zinc, and add warm freshly boiled water as the acid is permitted to flow out again. Close the stop with the water level above the zinc when all the acid has been displaced, as indicated by litmus paper test. The zinc is good for about 6 determinations, when it should be removed, thoroughly cleaned, and again amalgamated, or the reductor filled with new zinc freshly amalgamated.

### Procedure

**Solution of the Sample and Separation of Cb and Ta.**—Transfer 2 g of the sample (or up to 5 g if Cb or Ta is low) to a covered beaker and add 20 ml of HCl (sp. gr. 1.19) and 10 ml of HNO<sub>3</sub> (sp. gr. 1.42). Heat to 90° C until the cuttings have dissolved, and add 30 ml of HClO<sub>4</sub> (60-per cent). For a larger sample, increase the volumes of all these acids added proportionately. Boil the solution down to fumes, and continue the heating for 5 minutes with HClO<sub>4</sub> condensing upon and flowing down the inner wall of the beaker to oxidize the chromium completely. Cool the beaker somewhat and add 200 ml of hot water, 10 ml of HCl, and 60 ml of H<sub>2</sub>SO<sub>3</sub> solution. Boil 3 minutes, add some ashless paper pulp, and digest at 60 to 70° C until the supernatant liquid is clear, usually 15 to 20 minutes. Fill the tip of an 11-cm filter paper with the paper pulp and filter the solution through it. Clean the beaker and wash the filter with hot dilute HCl (2-per cent) 12 to 15 times. Transfer the filter and contents to a 50-ml platinum dish and burn the paper completely at as low a temperature as practicable.

To purify the precipitate treat it as follows: Add about 5 ml of HF (48-per cent) and 10 ml of dilute H<sub>2</sub>SO<sub>4</sub> (1:1). Evaporate under a hot plate or in an air bath, and finally fume to a volume of 2 to 2.5 ml to expel all the HF. If the precipitate does not dissolve before the fuming stage is reached add 2 ml of HClO<sub>4</sub> (70-per cent) and continue the evaporation as directed. Transfer the solution to a 400-ml beaker with a stream of hot 2-per cent HCl, adding in all about 200 ml of the acid. Remove any precipitate adhering to the dish with a piece of filter paper moistened with the dilute HCl and add it to the beaker. Add 50 ml of H<sub>2</sub>SO<sub>3</sub> solution and boil several minutes. Introduce paper pulp, digest at 70° C for 15 minutes, and filter and wash as for the first precipitation. To remove any precipitate adhering to the beaker, clean it with filter paper moistened with the dilute HCl. Transfer the filter and precipitate to a clean, 30-ml, weighed platinum crucible, dry, and burn the paper at a low temperature, and finally ignite to constant weight at 1000° C to 1050° C. Cool and weigh as Cb<sub>2</sub>O<sub>5</sub> + Ta<sub>2</sub>O<sub>5</sub>.

**Determination of Columbium.**—Determine columbium by one of the methods:

1. Add to the crucible 2 to 3 g of K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> and fuse completely. Also, start a blank fusion and carry it through all subsequent steps of the analysis with the sample. Grasp the crucible with the tongs and spread the melt around the wall as it cools. Add 5 ml of H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84) and heat gently to a clear solution. Cool somewhat, and transfer the solution to a dry beaker, rinsing the crucible 3 times with 5 ml portions of H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84). Finally, rinse the crucible with

20 ml of 5-per cent solution of succinic acid containing 1 ml of 30-per cent  $\text{H}_2\text{O}_2$ , and cautiously add these rinsings to the beaker. Stir the solution thoroughly, dilute to 100 ml with cold water, and reserve for treatment as directed below.

Preheat the zinc column of the Jones reductor by passing 200 ml of water through it heated almost to boiling. Then connect the reductor to a 1000-ml suction flask containing 25 ml of ferric sulphate solution so that the delivery tube dips beneath the surface of the solution, and pass the following solutions through the tube in order: 150 ml of 20-per cent  $\text{H}_2\text{SO}_4$  solution heated to 60 to 70° C; the solution containing the columbium heated to the same temperature as the acid; 100 ml of 20-per cent  $\text{H}_2\text{SO}_4$  solution containing 1 g of dissolved succinic acid; and 150 ml of cold water, closing the stopcock before the top level of the water reaches the zinc. Transfer the solution in the flask to an 800-ml beaker and titrate immediately with the standard 0.05 *N*  $\text{KMnO}_4$  solution. Pass the blank through the reductor and titrate it in the same way as the sample. Subtract the ml of  $\text{KMnO}_4$  solution used to titrate the blank from the number of ml used to titrate the sample, multiply the difference by 0.002323, and divide the product by the weight of sample used and by 100 to find the per cent columbium.

To find the per cent of tantalum in the sample, multiply the ml of  $\text{KMnO}_4$  solution equivalent to the columbium present by 0.003323 or the total columbium by 1.4288; subtract this product, which gives  $\text{Cb}_2\text{O}_5$  in grams, from the weight of the mixed oxides; multiply the difference, which represents  $\text{Ta}_2\text{O}_5$ , by 81.91; and divide by the weight of sample used.

2. To determine columbium gravimetrically, transfer the mixed oxides to a platinum boat, and weigh the boat and contents carefully. Connect the tube of a combustion furnace heated to between 1000° and 1050° C with a  $\text{P}_2\text{O}_5$  tube, insert the boat into the cold end of the tube, and displace the air with dry hydrogen. When the weight of the  $\text{P}_2\text{O}_5$  tube becomes constant, push the boat into the hot zone with a disc-tipped rod inserted through the stopper, and withdraw the rod until the dish is in the cool end of the tube. Continue to pass the hydrogen until the weight of the  $\text{P}_2\text{O}_5$  tube becomes constant and for 10 minutes thereafter. Withdraw the tube from the furnace and continue to pass the hydrogen until the tube is cool. Remove the boat and weigh it rapidly. Subtract this weight from the original weight to find the weight of oxygen loss, which, multiplied by 5 and divided by 0.301, gives the weight of  $\text{Cb}_2\text{O}_5$ . Multiply the weight of  $\text{Cb}_2\text{O}_5$  by 69.90 and divide by the weight of sample to find the per cent columbium. Subtract the weight of  $\text{Cb}_2\text{O}_5$  from the weight of mixed oxides, multiply the difference by 81.91, and divide by the weight of sample to find the per cent of tantalum present.



**Procedure for the Determination of Columbium (Silicon and Tantalum) in Stainless and Heat-Resistant Steels: Presence or Absence of Selenium, Titanium, and Zirconium**

This method has for its chief object the determination of columbium alone and, though the combination is rare, also in the presence of moderate proportions of titanium such as are usually found in some types of stainless steels. Incidentally, silicon can also be accurately determined, and the presence of tantalum revealed. No special solutions or reagents are required. If zirconium is present or suspected and tantalum absent, the sample is analyzed by the method given under zirconium.

**Procedure**

**Solution of Sample and Separation of Silicon.**—Transfer 2 g of the sample to a 400-ml beaker, cover, and add 25 ml of perchloric acid (70-per cent) and 30 ml of hydrochloric acid. If selenium is present, endeavor to dissolve the sample in hydrochloric acid, by which treatment most of the selenium will be evolved as selenium sulfide and eliminated at this stage. Heat gently till the cuttings are dissolved, then boil until dense fumes of perchloric acid are evolved and are condensing on the wall of the beaker, and hold at this temperature 10 minutes to dehydrate the silicon completely. Proceed by one of the following plans according to whether or not it is desired to determine the silicon present, omitting the first if silicon is not desired.

**Determination of Silicon.**—Cool the fuming solution somewhat, add 150 ml of water, stir, filter immediately and as rapidly as possible on a close paper, and wash with hot water. Reserve the filtrate and treat at once as directed below for columbium. Transfer the filter, which holds practically all the silicon in the steel, some of the columbium, and all of the titanium, present in the steel as  $\text{TiO}_2$ , besides possible traces of other elements, to a weighed platinum crucible, and gradually ignite to about  $900^\circ \text{C}$ . Cool and weigh. Moisten the residue with 2 or 3 drops of dilute sulphuric acid (1:1), add 3 to 5 ml of hydrofluoric acid, evaporate carefully, and gradually ignite as before. Cool, weigh, and take the difference between the last two weights as silica. Multiply the weight of the  $\text{SiO}_2$  by 46.72 and divide by 2 to find the per cent silicon.

If the residue weighs more than 0.5 mg, scrub the crucible well and rinse into a small beaker with water, add a little perchloric acid, digest, dilute, add sulphurous acid, boil, filter and add to the quartz crucible, and ignite with the precipitate obtained below.

**Separation and Recovery of Columbium.**—Dilute the filtrate from the silica to 175-200 ml with hot water, stir in 30 ml of sulphurous acid ( $\text{H}_2\text{SO}_3$ ), place a small piece of filter paper under the stirring rod to avoid bumping, heat to boiling, and boil 10 minutes. Filter on a

close paper containing a little paper pulp, and discard the filtrate, which contains the iron and titanium. Place the paper and precipitate, which contains all of the columbium, except that in the residue from the volatilization of the silica, and is contaminated with iron and chromium, also with selenium, if present, in a quartz crucible with the filter containing the residue from the silica, and heat gently to char the paper. Ignite gradually to  $700^{\circ}\text{C}$  (a dull red) until all the carbon has been consumed. Cool the crucible, add 5 g of sodium pyrosulphate ( $\text{Na}_2\text{S}_2\text{O}_7$ ) and fuse for 10 minutes, or until the residue is dissolved. Cool the crucible, place it in the beaker, add 80 ml of water and 20 ml of hydrogen peroxide (3-per cent) to hold columbium and tantalum in solution, and heat gently until the melt has dissolved. Remove and rinse the crucible and cover, add 5 ml more of the  $\text{H}_2\text{O}_2$ , heat the contents of the beaker to boiling, and filter at once to remove silica and other impurities. Wash the filter 8 times with cold water, reserve the filtrate, and transfer the filter and contents to the platinum crucible used for volatilizing the silica.

Dry, char, and burn the paper. Add 2 ml of dilute sulphuric acid (1:1), 3 to 8 ml of hydrofluoric acid, and evaporate the latter acid and water slowly in an air bath or under a hot plate. Heat carefully till dense fumes of sulphuric acid are evolved, cool, rinse the wall of the crucible with a fine jet of water and again evaporate and heat to fumes, to make sure all the fluorides, which have a tendency to creep up the wall of the crucible, have been decomposed. Rinse the contents of the crucible into the filtrate from the fusion, and precipitate the columbium as directed below to free it of traces of interfering impurities, such as titanium.

Dilute the filtrate, which now contains all the columbium and possibly traces of titanium, iron, chromium, etc., to 300 ml, add 20 ml of perchloric acid (70-per cent), heat to boiling, and boil 10 minutes. Add 60 ml of sulphurous acid and continue the boiling 20 minutes. Stir in some paper pulp and filter through a close paper. Wash 6 times with cold water, 6 times with hot water, transfer the filter and contents to a weighed crucible, dry, and ignite gradually to  $1000^{\circ}\text{C}$ . Cool in a desiccator and weigh as  $\text{Cb}_2\text{O}_5$ . If tantalum and zirconium are known to be absent, multiply the increase in weight by 69.992 and divide by 2 to find the per cent columbium.

If zirconium is present or suspected and tantalum is present, fuse the ignited precipitate with  $\text{K}_2\text{CO}_3$ , leach with 50 ml of hot water, filter, wash with hot water, reserve the filtrate, ignite the residue gently, repeat the fusion and extraction, fuse with  $\text{K}_2\text{S}_2\text{O}_7$ , take up in dilute  $\text{H}_2\text{SO}_4$  (1:9), and determine zirconium by the phosphate or the phenylarsonate method. Subtract the weight of  $\text{ZrO}_2$  from the columbium. Treat the combined filtrates from the  $\text{K}_2\text{CO}_3$  fusion as directed below for the volumetric determination of columbium.

If tantalum alone is present or suspected, all or nearly all of it will be found with  $\text{Cb}_2\text{O}_5$ , and as a first step in their determination, fuse the ignited precipitate with 15 times its weight of  $\text{K}_2\text{S}_2\text{O}_7$ . Cool, add 10 ml of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84), and heat gently until the melt dissolves. Transfer to a dry beaker, rinse the crucible with 30 ml of  $\text{H}_2\text{SO}_4$ , dilute to 200 ml, and determine columbium by reducing in a Jones reductor and titrating with 0.05 *N*  $\text{KMnO}_4$  solution as directed in the succeeding method for both elements. One ml equals 0.002323 g Cb. Using the factor 1.4288, calculate Cb to  $\text{Cb}_2\text{O}_5$ , subtract from the weight obtained above, and multiply the difference,  $\text{Ta}_2\text{O}_5$ , by 81.94 and divide by 2 to find the per cent tantalum.

### Procedure for the Determination of Tantalum (and Columbium)

#### Solution and Separation of Iron, etc.

Transfer 2 to 5 g of sample, according to the expected percentage of tantalum present, to a 400-ml beaker, add 100 ml of dilute hydrochloric acid (1:4) for each gram of sample or less, and heat gently until the metal dissolves. Collect the insoluble matter, which contains most, if not all, of the tantalum, according to proportions of certain other elements present, and wash with dilute hydrochloric acid (5-per cent). Reserve the residue and treat the filtrate for the recovery of any trace of tantalum as follows:

To reduce all the iron in the solution, add a few ml of a solution containing 1 to 2 g of sodium sulphite ( $\text{Na}_2\text{SO}_3$ ), stir, heat to boiling, and add ammonia slowly with constant stirring until a dark colored permanent precipitate of ferrous hydroxide barely forms. Avoid an excess of ammonia to keep the amount of iron precipitated as small as possible. Filter rapidly, wash with hot water, and discard the filtrate. If much iron has been precipitated, dissolve with  $\text{HCl}$  (1:4), add  $\text{Na}_2\text{SO}_3$ , reprecipitate as before, and filter through the same paper.

Transfer the filters to a quartz or porcelain crucible, dry, and gradually ignite to 600° C. Fuse the gently ignited residue with 5 to 8 g of  $\text{KHSO}_4$ , cool, and place the crucible in the original beaker with 50-100 ml of hot water containing 5 to 10 g of tartaric acid. When the fusion has dissolved, filter, wash with water, reserve the filtrate, and ignite the residue gently as before. Treat with  $\text{H}_2\text{SO}_4$  and  $\text{HF}$  to volatilize silica, fuse again with a little  $\text{KHSO}_4$ , and dissolve in the filtrate. Cool and pass  $\text{H}_2\text{S}$ . If sulphur forms, as it generally does, filter, wash with a 5-per cent solution of ammonium chloride, and discard the filter.

To remove all the iron, stir in paper pulp, add ammonia till alkaline, and pass  $\text{H}_2\text{S}$ . When the precipitate has fully formed, filter, wash thoroughly with the 5-per cent  $\text{NH}_4\text{Cl}$  solution, and discard the filter and precipitate.

### Separation and Determination of Tantalum

Boil the filtrate to remove  $\text{H}_2\text{S}$ , add a measured portion of dilute  $\text{H}_2\text{SO}_4$  (1:1), and boil down until the solution contains 10 per cent  $\text{H}_2\text{SO}_4$ . If any tantalum is precipitated by hydrolysis in this process, filter the solution, wash the beaker and filter with 5-per cent ammonium chloride, and reserve the filter for ignition later.

To the clear solution cooled to 15 to 20° C, add 45 ml of a freshly prepared solution containing 3 g of cupferron, stirring constantly while making this addition. Filter with the aid of paper pulp and wash with a 2-per cent solution of cupferron.

Transfer the 2 filters to a porcelain crucible, dry, and gradually ignite to about 1000° C. Carefully brush the residue into a small beaker, add 10 ml of dilute hydrochloric acid (5-per cent), boil 5 or 6 minutes, filter, and wash as before. Ignite the filter in a weighed platinum crucible, cool, and weigh as  $\text{Ta}_2\text{O}_5 + \text{Cb}_2\text{O}_5$ , if columbium is present. In the absence of columbium, multiply by 81.94 and divide by the weight of sample used to find the per cent tantalum.

To test for columbium, fuse with  $\text{K}_2\text{S}_2\text{O}_7$ , dissolve in  $\text{H}_2\text{SO}_4$ , titrate as directed in the following method, calculate Cb to  $\text{Cb}_2\text{O}_5$ , and subtract from the weight of  $\text{Ta}_2\text{O}_5$ .

### Method for Columbium and Tantalum, Titanium, and Zirconium

In the following procedure, an attempt has been made to provide a method for determining columbium, tantalum, and zirconium in any type of steel. In analyzing known steels many of the steps outlined may be omitted.

**Special Solutions and Apparatus Required** are the same as those given in the preceding method.

**Weight of Sample.**—The weight of sample is varied according to the lowest percentage of either columbium or tantalum present—1 g for 2 per cent or more, 2 g for 0.5 per cent to 2 per cent, and 5 g for lower percentages.

### Procedure

**Solution of Sample and Separation of Cb, Ta, Ti, and Zr.**—*Absence of Tungsten.*—Dissolve the sample in dilute  $\text{HCl}$  (1:1) or in dilute  $\text{H}_2\text{SO}_4$  (1:4), using the former preferably, and heating gently to hasten solution. Filter rapidly, and wash the beaker and filter with dilute  $\text{HCl}$  (1:4). Reserve the residue and treat the filtrate for the precipitation of portions of these elements that remain in solution, as follows:

Separate most of the iron by either of the following methods. (a) Add  $\text{HNO}_3$  to oxidize the iron, evaporate to the first signs of crystallization, add 50 ml of  $\text{HCl}$ , evaporate again to expel all the  $\text{HNO}_3$ ,

dilute with 10-per cent HCl, and filter. Wash the filter with water and reserve. Evaporate the filtrate again, take up in HCl (sp. gr. 1.19), and make an ether separation as directed under *Chemical Separations*. Evaporate and boil off the ether from the acid solution. In the absence of chromium or vanadium, dilute, precipitate with ammonia, wash with water, and reserve the filter. In the presence of chromium, add 10 to 20 ml of  $\text{HClO}_4$ , fume to oxidize  $\text{Cr}^{\text{IV}}$  to  $\text{Cr}^{\text{VI}}$ , precipitate with ammonia, wash, and filter. Add the 2 filters and their contents to the first, and treat all as directed below.

(b) Add a solution of  $\text{SO}_2$  or  $\text{Na}_2\text{SO}_3$  to reduce all the iron, expel any excess of  $\text{SO}_2$  by boiling, and add ammonia with constant stirring until a dark-colored precipitate appears that does not dissolve on continued stirring. Filter rapidly, wash 2 or 3 times with hot water, and discard the filtrate. If too much iron was precipitated, dissolve with hot dilute HCl (1:4), wash with water, reserve the filter; and reprecipitate, filter, and wash as before.

Transfer the three papers to a porcelain or quartz crucible, dry, and gradually ignite to  $600^\circ \text{C}$ . Fuse with 5 to 8 g of  $\text{KHSO}_4$ , place the crucible in the beaker in which the first partial separation or precipitation was made with 50 to 100 ml of hot water containing 5 to 10 g of tartaric acid, and heat gently till the fusion has dissolved. Filter, wash with water, reserve the filtrate, ignite, and treat the residue, if any, with  $\text{H}_2\text{SO}_4$  and HF to volatilize silica. Fuse the residue with a little  $\text{KHSO}_4$  and dissolve the melt in the filtrate. Cool and pass  $\text{H}_2\text{S}$  to reduce iron, etc., and filter off any sulphur formed. Wash the filter with 5-per cent  $\text{NH}_4\text{Cl}$  solution and discard the filter. To remove all the iron, stir in paper pulp, add ammonia till decidedly alkaline, and pass  $\text{H}_2\text{S}$ . Digest at  $40^\circ \text{C}$  for 20 to 30 minutes. Filter, wash with 5-per cent  $\text{NH}_4\text{Cl}$  solution, and discard the filter and precipitate.

Acidify the filtrate with  $\text{H}_2\text{SO}_4$ , add an excess of 10 ml per 100 ml of solution, and boil to expel  $\text{H}_2\text{S}$ . Cool to below  $20^\circ \text{C}$ , add paper pulp, and precipitate with a 6-per cent solution of cupferron as directed under *Chemical Separations*. Filter and wash with cold dilute HCl (10-per cent) to which a little cupferron solution has been added. Discard the filtrate and transfer the paper and precipitate to a weighed platinum crucible. Ignite slowly till the paper has burned, and, if it is thought necessary, volatilize silica with  $\text{H}_2\text{SO}_4$  and HF. Finally, ignite gradually to  $1100^\circ \text{C}$ , and weigh as  $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5 + \text{TiO}_2 + \text{ZrO}_2$ .

*Presence of Tungsten.*—The following procedure is one of the older methods for separating tungsten from zirconium, columbium, tantalum, and titanium. We have not been able to apply the method with certainty, and prefer the procedure given under zirconium. However, as the method was checked by only one laboratory during the course of our investigations to the time of this publication, we are outlining the procedure as a convenience for future investigations.

Dissolve the sample in dilute HCl (1:1), and add  $\text{HNO}_3$  dropwise to decompose carbides and oxidize the tungsten. Dilute with 3 to 4 volumes of water, boil 5 minutes, filter, and wash with 1-per cent HCl. Reserve the paper and insoluble matter. Expel the nitric acid from the filtrate by adding 50 ml HCl and evaporating to a syrupy consistency. Repeat the addition of HCl and evaporation, and filter if necessary to remove silica, which should be volatilized and any residues reserved. Then make an ether extraction as directed under *Chemical Separations*. Boil the acid solution from the ether extraction to expel the ether completely, add 10 ml of perchloric acid (70-per cent), and fume to oxidize chromium. Cool, dilute, precipitate by neutralizing with ammonia, filter, wash with hot water, and discard the filtrate. Avoid adding an excess of ammonia in this precipitation else some columbium will not be completely precipitated.

Transfer the papers to a platinum crucible, burn the papers at a low temperature, and fuse the residue with  $\text{K}_2\text{S}_2\text{O}_7$ . Dissolve the melt in water, and digest with HCl and  $\text{HNO}_3$  to oxidize the tungsten. Dilute to 200 ml, heat to boiling, and add just enough of a 25-per cent solution of NaOH to dissolve the tungstic acid. Add HCl till acid to litmus, add NaOH till the solution is just alkaline to litmus, and add 2 or 3 drops in excess. Boil 1 minute, filter, wash with hot water, and discard the filtrate. Note: We believe some Cb is lost here, being held in solution with the tungsten by the NaOH. Place another beaker under the funnel, and wash the filter with hot dilute HCl (1:4) and hot water, but do not discard it. Treat the solution with NaOH, filter, and wash as before. Place all the papers in a porcelain crucible, dry, ignite gently, fuse with  $\text{KHSO}_4$ , and complete the separation as directed above.

**Separation of the Elements in the Mixed Oxides.**—To separate zirconium, fuse the mixed oxides with  $\text{K}_2\text{CO}_3$ , leach with hot water, filter, and wash. If there is a residue, ignite at a very low temperature, and repeat the fusion and extraction with water, combining all filtrates and washings. Reserve the latter, and ignite and fuse the residue with  $\text{K}_2\text{S}_2\text{O}_7$ . Take up in dilute  $\text{H}_2\text{SO}_4$ , add hydrogen peroxide, determine titanium by color, and complete the determination of zirconium by precipitating as phosphate or with phenylarsonic acid as directed under methods for zirconium.

**Determination of Titanium.**—Since fusion with  $\text{K}_2\text{CO}_3$  leaves most of the titanium in solution, acidify the filtrates with  $\text{H}_2\text{SO}_4$ , add  $\text{H}_2\text{O}_2$ , and compare with a standard solution containing a like amount of potassium salts. Add the titanium formed with the zirconium, and divide by the weight of sample used in calculating the per cent titanium in the sample. If zirconium is absent, fuse the mixed oxides with a little  $\text{K}_2\text{S}_2\text{O}_7$ , take up in dilute sulphuric acid, and determine all the titanium together by color.

**Determination of Columbium.**—To the filtrate from the separation of zirconium, or the solution of  $K_2S_2O_7$  fusion, add an excess of  $H_2O_2$ , separate columbium and tantalum with  $SO_2$ , and determine the former by reduction with zinc and titration with permanganate as directed in the standard procedure for these two elements.

#### Text References

1. Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel," 1st Ed., New York, John Wiley and Sons, Inc., 1931.
2. Silverman, L., *Ind. Eng. Chem. (Anal. Ed.)*, 6, 287 (1936).
3. Cunningham, T. R., Analysis of 18-Per Cent Chromium-8-Per Cent Nickel Steel Determination of Columbium and Tantalum. Electro Metallurgical Company, *Private Communications*.

# Determination of Selenium

Selenium is determined either gravimetrically or volumetrically. In the gravimetric methods, which until recently were the only methods available, the selenium is separated and weighed in elementary form. As these procedures are subject to certain inherent sources of error difficult to overcome, a study of methods for determining selenium and tellurium was begun at Duquesne Works Laboratory in the fall of 1932, and the third of the volumetric methods given below was developed for carbon and stainless steels, to be followed early in 1936 by that of Marvin and Schumb<sup>1</sup> for stainless steels, the procedure for which is also given. Study of these methods led to the development by South Works Laboratory of the Standard Volumetric Method for Stainless Steels, which was reported December 8, 1936, and is given below.

## Standard Volumetric Method for Stainless Steels, Selenium Being Separated with $\text{SO}_2$ and Titrated with $\text{KI}$ and Sodium Thiosulphate

The following procedure has been proved accurate when applied to selenium-bearing stainless steels. It combines the best principles of the gravimetric methods for separating selenium, and of the volumetric methods already given for determining it.

### Special Solutions and Reagents Required

**Special Reagent.**—C. P. urea. Used in solid form.

**Starch Solution.**—Mix 5 g of good starch with water to form a thin paste and stir into 500 ml of boiling water. Cool, decant clear solution, and use while fresh.

**Standard Sodium Thiosulphate Solution, 0.05 N.**—Dissolve 12.5 g of pure  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in freshly boiled distilled water, add 0.1 g of  $\text{Na}_2\text{CO}_3$ , and dilute to 1 liter.

Since a normal solution is equivalent to 19.74 g of Se per liter, 1 ml of 0.05 N solution is equivalent to 0.1974 per cent on 5 g of sample. The solution is standardized in the usual manner against 0.05 N permanganate solution, which is in turn standardized against sodium oxalate. The thiosulphate solution is not stable and should be checked each day it is used against  $\text{KMnO}_4$  solution.

**Standard Iodine Solution, 0.05 N.**—Weigh 6.347 g of pure iodine in a weighing bottle, dissolve with 35 ml of water containing 25 g  $\text{KI}$  (free of  $\text{KIO}_3$ ), transfer to a 1-liter volumetric flask partly filled with water,



mix, and dilute to the mark. The solution is convenient for back-titrating thiosulphate, and may be substituted for permanganate.

**Hydrochloric-Sulphurous Acid Solution.**—Saturate the concentrated acid with  $\text{SO}_2$ , produced in a generator by treating  $\text{Na}_2\text{SO}_3$  with dilute  $\text{H}_2\text{SO}_4$  (1:1).

### Procedure

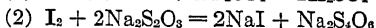
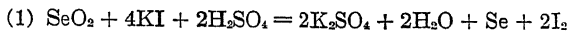
**Solution of Sample and Separation of Selenium.**—Transfer 5 g of sample to a 400-ml beaker, add a mixture of 30 ml of  $\text{HCl}$  and 30 ml of  $\text{HNO}_3$  all at once, cover, and allow the first violent action, which may be slow in starting, to subside. Then heat to  $60^\circ \text{C}$  until the sample is dissolved, add 30 ml of perchloric acid (70-per cent), and evaporate to fumes. If the steel is high in chromium, heat till the chromium is oxidized as indicated by the color, or for 5 minutes after the acid is condensing on the wall of the beaker, if the steel contains little or no chromium. Cool, rinse the wall of the beaker with cold water, and dilute to 100 ml. Heat gently to dissolve salts and add 125 ml of hydrochloric acid saturated with  $\text{SO}_2$  and 60 ml of sulphurous acid. Stir, heat to  $90^\circ \text{C}$ , hold at this temperature for 1 hour, stirring occasionally. Filter through a thin, close pad of asbestos supported by a Gooch crucible, and wash the beaker, the separated selenium, and the filter with hot water.

**Solution and Titration of Selenium.**—Transfer the crucible and pad containing the selenium to the original beaker, add 40 ml of  $\text{HNO}_3$ , and evaporate to a volume of 10 to 15 ml. Remove the crucible, rinsing it thoroughly with hot water. To remove iron, add ammonia until the solution is slightly alkaline, heat, filter, and wash with hot water. Neutralize the filtrate with nitric acid and add 10 ml excess. Heat to  $60^\circ \text{C}$ , add 3 g of urea, stir, and cool to room temperature. Add 3 g of potassium iodide, stir for 3 minutes, and add a small excess of 0.05 *N* sodium thiosulphate solution over that required to react with the liberated iodine. Add 5 ml of starch solution and back-titrate the excess iodine with standard permanganate solution to a fixed blue end point. Subtract to find the ml of thiosulphate or permanganate equivalent to the selenium present and from the factors given above calculate the per cent selenium.

## Volumetric Methods

### Hydrogen Chloride-Bromide-Iodide Method

In this method, the sample is dissolved in  $\text{HCl}$ , the Se evolved as  $\text{H}_2\text{Se}$  is collected in a solution of  $\text{KOH}$  and  $\text{Br}$ , that not evolved is treated with  $\text{Br}$ , the whole of the  $\text{H}_2\text{SeO}_4$  is reduced to  $\text{SeO}_2$  with  $\text{HBr}$ , the  $\text{SeO}_2$  in sulphuric acid solution is reduced to Se by adding  $\text{KI}$ , and the iodine liberated is titrated with standard sodium thiosulphate solution in accordance with the following reactions:



Success with the method depends upon maintenance of proper conditions, particularly in the first steps of the analysis. When carefully carried out in accordance with directions as given below, it gives satisfactory results.

**Special Apparatus and Reagents Required.**—The apparatus is similar to that employed for the determination of sulphur by the volumetric evolution method.

Fit a 300-ml Erlenmeyer flask with a 2-hole rubber stopper, and bend a glass tube to extend from 1 hole of the stopper in the flask to the bottom of a 10"  $\times$  1" test tube. Through the other hole of the stopper insert the stem of a separatory bulb with stopcock so that the tip of the stem almost touches the bottom of the flask with the stopper in place. Fit the opening of the separatory bulb with a 1-hole stopper bearing a glass tube bent at a right angle for connection to a supply of hydrogen or sulphur-free natural gas for aspirating. Set up the apparatus so that heat may be applied as desired to the bottom of the flask and connect with the supply of gas for aspirating. Also, have at hand a second 10"  $\times$  1" test tube.

The reagents required include bromine water, a 0.5-per cent solution of potassium hydroxide (KOH), concentrated and dilute hydrochloric acid (1:1), sodium sulphite solution (25-per cent, freshly prepared), dilute sulphuric acid (1:1), potassium iodide solution (8-per cent), standard 0.02 *N* sodium thiosulphate solution, and standard (approximately 0.02 *N*) iodine solution. The thiosulphate is standardized in the usual manner against Bureau of Standards sodium oxalate through potassium permanganate solution. The iodine solution is used for back-titrating, and its relation to the thiosulphate solution must be carefully established by titrating the same amounts of the latter in the same volume as in a regular determination.

**Procedure.**—With the apparatus and reagents in readiness, transfer 5 g of sample to the Erlenmeyer flask, and add to the 10-inch test tube 10 ml of the 0.5-per cent KOH solution, 20 ml of bromine water, and 30 ml of water. Connect the apparatus and transfer to the separatory bulb 40 ml of dilute HCl (1:1) and 50 ml of concentrated HCl. Admit the acid to the flask, displace the air in the flask with the aspirating gas, and apply heat till the solution is warm, to hasten solution of the sample, but not enough to boil off the acid. When the sample has dissolved, increase the temperature somewhat, but do not boil, and pass hydrogen or sulphur-free natural gas through the apparatus until all the gas generated during solution of the steel has been displaced, adding more bromine if necessary to keep the solution slightly colored with it.

In the meantime, transfer 20 ml of the sodium sulphite solution to the extra 10-inch tube and place it alongside the one containing the bromine solution. Now, raise the flask while aspirating slowly; quickly rinse the outside of the delivery tube that dipped into the bromine solution and insert it into the tube containing the sodium sulphite solution; shut off the aspirating gas; close the stopcock on the separatory bulb; and permit the flask to cool somewhat, sucking the sulphite solution into the flask and partly filling the latter with  $\text{SO}_2$  gas. Shake the flask occasionally as it cools, and while it is still warm, remove the stopper, rinse all parts, collecting the rinsings in the flask, and also transfer the remaining sulphite solution to the flask. Stopper and shake the flask for 1 or 2 minutes, and filter the solution through a close asbestos mat supported in a Gooch crucible, transferring and washing the residue with dilute  $\text{HCl}$  (1:1).

By these operations any selenium, not evolved as  $\text{H}_2\text{Se}$  and collected in the bromine solution, is reduced to elementary selenium by the  $\text{SO}_2$  and collected upon the filter, provided the proper concentration of the  $\text{HCl}$  in the flask has been maintained, as will be the result if directions above are carefully followed.

The next step includes oxidation of the selenium to  $\text{H}_2\text{SeO}_4$  with bromine, and its subsequent reduction with  $\text{HBr}$  to  $\text{H}_2\text{SeO}_3$ , an operation that also requires careful attention to details.

To this end, first mark a 250-ml beaker at the 75 ml level, transfer the crucible to it, and pour 15 ml of bromine water into the crucible. Let it stand while the bromine water seeps through, and warm gently, if necessary, to dissolve any dark-colored particles. When the grayish residue has dissolved, remove the crucible and wash it thoroughly, holding the volume between 80 and 90 ml. Then transfer the contents of the bromine tube to the beaker and rinse it thoroughly with 40 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1). Boil gently and continue heating until the solution has evaporated to the 75-ml mark.

Cool the solution, transfer it to a 600-ml beaker, rinsing the smaller beaker with 25 ml of water. To reduce the  $\text{H}_2\text{SeO}_3$  to  $\text{Se}$ , agitate the solution, add 20 ml of the 8-per cent solution of  $\text{KI}$ , let the mixture stand 20 seconds, and dilute to 400 ml with water.

If selenium is present, the solution will be colored to a depth corresponding to the percentage present, due to the finely precipitated "red" selenium and the liberated iodine.

Add the standard sodium thiosulphate solution, observing the solution closely, until the color due to iodine fades. To obtain an end point most readily reproducible, complete the determination as follows, although the back-titration may not be necessary. Then add an excess of 5 to 6 ml, stir, and add 5 ml of good fresh starch solution containing no preservative of any kind. Back-titrate the excess of thiosulphate

solution to the established blue end point. Subtract the thiosulphate equivalent of the iodine used from the total ml of the sodium thiosulphate to find the ml of the latter equivalent to the iodine liberated. From the normality of the thiosulphate solution present, calculate the per cent selenium present.

From the reactions previously given, it is evident that a liter of a normal solution is equivalent to 19.74 g of Se. Therefore, the selenium titer of 1 ml of the sodium thiosulphate solution equals the normality factor multiplied by 0.01974. With a 5-g sample  $0.3948 \times$  the normality gives the Se value of 1 ml in per cent.

### **The Perchloric-Nitric Acid-Iodide Method for Stainless Steels. Method of Marvin and Schumb**

**Procedure**—Transfer 5 g of sample to a 250-ml Erlenmeyer flask, equipped with a 1-hole rubber stopper carrying a small drying tube, in the larger end of which is a pad of glass wool about 1 inch long. Add 30 ml of water and 40 to 50 ml of perchloric acid (60-per cent), and close the flask with the stopper. Pour 3 or 4 drops of nitric acid upon the glass wool to retain the  $\text{H}_2\text{Se}$  evolved at the start of the reaction, heat the flask and contents to between  $80^\circ$  and  $85^\circ$  C, and set aside until solution is complete.

At any time after 2 minutes, remove the drying tube, extract the pad of glass wool, containing all the Se evolved as  $\text{H}_2\text{Se}$ , place it in a beaker, and rinse the tube with concentrated nitric acid, permitting the acid to flow into the beaker with the glass wool.

Now, filter the solution of the steel through a close asbestos filter pad, using suction, and wash 2 or 3 times with warm water. Transfer the pad and precipitate to the beaker containing the glass wool plug, and wash the filter tube thoroughly with 30 to 40 ml of nitric acid, collecting all of this acid in the beaker also. Digest and evaporate to about 15 ml. Add ammonia until the solution is barely alkaline to precipitate iron, etc., filter, and wash the residue thoroughly with hot water. Neutralize with dilute nitric acid and add 10 ml of concentrated acid, both free of nitrous fumes. To make sure no nitrous fumes are present, heat to  $60^\circ$  C, and add 2 g of urea. Cool the solution to room temperature and dilute to 400 ml. Add a concentrated solution containing 3 g of potassium iodide, let the mixture stand 1 to 2 minutes, and titrate the liberated iodine with standard sodium thiosulphate solution as directed in the preceding method.

### **Gravimetric Methods**

There are several gravimetric methods for selenium, four of which are given below. The first is the only one that provides for possible interference by tellurium, and it is, therefore, recommended as a referee method when the presence of tellurium is known or suspected.

**Iodine Solution-HClO<sub>4</sub>-SO<sub>2</sub> Method in Presence of Tellurium**

In this method the sample is dissolved with iodine, and the selenium is oxidized with perchloric acid and precipitated in hydrochloric acid solution with SO<sub>2</sub>.

**Procedure.**—Transfer 25 g of sample (a smaller sample can be used but with less accuracy) to a 400-ml beaker, add 125 ml of water, and dissolve the metal by adding gradually a total of 130 g of iodine.

The steel dissolves readily, leaving a residue of oxides, selenides, and elementary selenium. Tellurium, if present, dissolves.

Collect the residue upon a close paper filter and wash with a 10-per cent solution of potassium iodide until free of ferric iodide, then wash a few times with water to remove the KI. If the selenium is to be reduced later with hydroxylamine hydrochloride, use a filter of frit glass, porosity No. 1, instead of the paper. Place the filter paper in the flask of an all-glass Soxhlet extraction apparatus, the thimble compartment of which is filled with glass beads, the thimble being omitted. Transfer 20 ml of perchloric acid (70-per cent) to the flask, and apply heat gently until the paper is destroyed. When condensate appears in the thimble compartment and the perchloric acid is fuming strongly, allow the flask to cool somewhat, disconnect the Soxhlet condenser, and rinse the connections into the flask. Then, rinse the inside of the condenser with concentrated hydrochloric acid into the thimble compartment, disconnect, and rinse it and the connections once with water, using as little water as possible. Finally, pour concentrated hydrochloric acid down the sides of and over the beads in the thimble compartment, until there is enough to start the automatic siphon and permit the washings to flow into the flask. Then rinse the distilling tube on the side of the thimble compartment with concentrated hydrochloric acid, permitting it to flow into the flask.

In this way all traces of selenium are gathered in the solution in the flask, which should not exceed 90 ml in volume. It may be treated for the separation and determination of the selenium by either of the two following methods, of which the first is recommended.

**Precipitation of Se by the HCl-SO<sub>2</sub> Method: Absence of Tellurium**

Filter the contents of the flask through glass frit or an alundum crucible, and wash the latter with concentrated hydrochloric acid, using 10 to 15 ml. To precipitate the selenium, saturate 50 ml of cold concentrated hydrochloric acid with SO<sub>2</sub> and stir it slowly into the solution containing the selenium. Allow the solution to stand until the red selenium subsides and filter through a weighed Gooch crucible provided with a tight asbestos pad. Wash the crucible and precipitate thoroughly with cold concentrated hydrochloric acid, then with water until the washings give no precipitate when added to silver nitrate solution, next with alcohol to replace the water, and finally 2 or 3 times

with ether. Dry for 3 hours at 30° to 40° C, and finally, at 120° to 130° C for 30 minutes. Cool and weigh as selenium. To convert the results to per cent, multiply by 100 and divide by the weight of sample used.

#### **Precipitation of Se by the Iodine-Citric Acid-Hydroxylamine Hydrochloride Method: Presence of Tellurium**

In this method the sample is dissolved with iodine as in the preceding method, but the residue is collected upon a glass frit filter.

Place the filter in a 100-ml beaker and dissolve the selenium with a small quantity of dilute nitric acid (sp. gr. 1.25). Remove and rinse the crucible with water. Evaporate the solution just to dryness, finishing on a water bath, to remove nitric acid and avoid loss of selenium. Dissolve the residue with as little sodium hydroxide solution (5-per cent) as possible, and add a 5-per cent solution of citric acid to make a volume of 100 ml. Add 10 ml of a 25-per cent solution of hydroxylamine hydrochloride and digest for 4 hours at a temperature of 90° C. Collect the black granular precipitate of elementary selenium upon a weighed Gooch crucible, wash with hot water, then with alcohol, and dry for 1 hour at 105° to 110° C. The net weight multiplied by 100 and divided by the weight of sample used gives the per cent selenium.

#### **Methods Involving Solution in Acids, Precipitation with SO<sub>2</sub> and Volatilization of Selenium**

**Solution of Sample and Separation of Selenium.**—Transfer 5 g to 10 g of the sample to a 600-ml Erlenmeyer flask or a covered 400-ml beaker. Add 50 ml to 60 ml of a mixture of equal parts of concentrated HCl and HNO<sub>3</sub>. If the initial reaction is violent, cool in running water. When solution is complete, treat by either of the following methods: (a) Add 35 ml of perchloric acid (70-per cent) and evaporate rapidly till red chromic acid crystals separate or until perchloric acid vapors begin to condense near the top of the beaker or flask. Cool slowly, cautiously add 100 ml of cold water, and agitate until separated salts are dissolved. To remove silica, cool, filter through a close paper, and wash with warm dilute HCl (1:1) and warm water to a volume between 150 and 175 ml. Add HCl equal to 70 per cent of the solution, follow with 100 ml of H<sub>2</sub>O freshly saturated with SO<sub>2</sub>, warm to 65° C (150° F), and allow to stand 8 to 12 hours at this temperature. Cool to below 50° F and separate the selenium as directed below.

(b) Evaporate the mixed acid solution to dryness on a water bath. Do not bake. Add 10 ml HCl (1:1) and 20 ml cold water, stir, and digest on a water bath till salts have dissolved. Filter through a close paper, wash 2 or 3 times with dilute HCl (1:1), and finally with water till free of chlorides. Discard the residue and dilute filtrate and

washings to about 150 ml with cold water. Add concentrated HCl equal to 70 per cent of the volume of the solution (about 100 ml) and pass a current of washed  $\text{SO}_2$  gas through the solution at the rate of about 2 small bubbles per second, holding the temperature at  $65^\circ$  to  $70^\circ$  F (room temperature) and stirring frequently to granulate the selenium. After all the selenium has been precipitated and the solution saturated with  $\text{SO}_2$ , allow the precipitate to settle for 1 hour, then filter as directed below.

**Purification and Determination of Selenium.**—As a filter for collecting and weighing the selenium, prepare a Gooch crucible with thoroughly purified and washed asbestos of the amphibole variety, which has been dried and ignited at a temperature of  $700^\circ$  C or higher. After the filter has been prepared, dry, ignite at  $700^\circ$  C, cool, and weigh. Wash with water, dry at  $90^\circ$  C, and reweigh to check loss on ignition. Filter the solution containing the selenium through the crucible, washing the selenium upon the filter with warm dilute HCl (1:1). Then wash free of acid with warm water, 2 or 3 times with ethyl alcohol (95-per cent), and once with ether. Dry the crucible in an air bath at  $85^\circ$  to  $90^\circ$  C and weigh. Record the gain in weight as selenium. To check the purity, ignite to constant weight at a temperature no higher than necessary to volatilize Se ( $690^\circ$  C), cool, and weigh. If this weight is within 1 mg of the ignited weight of the empty crucible, and the asbestos mat shows no marked discoloration, consider the selenium pure. Otherwise subtract the ignited weight of the crucible after volatilizing the selenium and record the difference as pure selenium. Divide the weight of pure selenium by the weight of sample taken to find the per cent selenium.

### Copper Chloride-Perchloric Acid Method

This method developed by Louis Silverman<sup>2</sup> is an adaptation of Meineke's method for sulphur, the solution in the acid copper chloride separating carbon, sulphur and selenium from most of the iron, chromium, silica, etc. As to accuracy, the method gives results comparable with other gravimetric methods.

**Special Solutions Required.**—*Zinc Oxide-Nitric Acid Reagent.*—Sift 20 g of zinc oxide into 100 ml of nitric acid.

*Copper-Potassium Chloride Solution.*—Dissolve 500 g of  $2\text{KCl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 2000 ml water and 100 ml of hydrochloric acid.

**Procedure.**—Transfer 5 g of the steel to a 600-ml beaker, add 500 ml of the copper chloride solution, place the beaker on a steam bath, and stir frequently. When all metallic particles (copper) have dissolved, gather the residue on a filter paper, wash with hot water, and return the paper to the beaker. Add 10 ml of the zinc oxide-treated nitric acid, 50 ml of water, 15 to 20 ml of perchloric acid (70-per cent), and evaporate to fumes. When the chromium is oxidized, as indicated

by the color change, cool the beaker, and, while shaking, gradually add 50 ml of water. Boil to expel chlorine, filter off silica, and wash with dilute hydrochloric acid (1:1) and water. Adjust the volume to 100 to 125 ml, and add an equal volume of hydrochloric acid and 100 ml of a freshly prepared saturated solution of  $\text{SO}_2$ . Let the beaker stand on a steam bath for 3 hours. Collect the selenium upon a close filter pad of purified and ignited asbestos, wash with dilute hydrochloric acid (1:1), then with water, and dry at  $100^\circ \text{C}$  for 1 hour. Cool, weigh, ignite at  $600^\circ \text{C}$ , cool, and weigh again. Subtract this weight from the first to find the weight of selenium in the sample, which is converted to per cent by multiplying by 100 and dividing by 5, the weight of the sample taken.

#### Text References

1. Marvin, G. G., and Schumb, W. C., *Ind. Eng. Chem. (Anal. Ed.)*, **8**, 109 (1936).
2. Silverman, L., *ibid.*, 132.



# Determination of Boron

## Occurrence of Boron

Boron is seldom added to steel except for experimental purposes. However, it is widely distributed and occurs in some iron ores, particularly those of the Lake Superior District. Just what happens to the boron when these ores are reduced in the blast furnace is unknown. Some "treatments" in which borax is used may result in the reduction and absorption of a little boron. As a matter of fact, however, so few tests have been made that it is not possible to say how widely it may be distributed in steel. In dissolving steels in acids, it is probably converted to boric acid, which partly escapes with steam on boiling. Its fluoride,  $\text{BF}_3$ , is volatile, and since boric acid is carried down with silicic acid, it may cause high results for silicon.

During the year 1936, several alloys of boron were marketed. One of these is said to be a blend of low-carbon steel and metallic boride crystals. Introduction of the boride crystals into low-carbon steel in a certain proportion is said to give a close-grained type of steel with a Brinell hardness of 682 in the cast condition. This alloy can be annealed for machining and subsequently hardened to almost the cast hardness to give a metal showing exceptional hardness, great strength, and high resistance to abrasion and corrosion.

It is, therefore, important that methods for its determination receive due attention.

## Methods Available

Four methods for its determination in iron and steel are described by Lundell, Hoffman, and Bright (see "Chemical Analysis of Iron and Steel," New York, John Wiley and Sons, Inc., 1931). One depends upon the volatility of methyl borate,  $\text{B}(\text{OCH}_3)_3$ , which boric acid forms with methyl alcohol; a second upon its separation with  $\text{CaCO}_3$ ; a third on its separation by electrolysis over a mercury cathode; and the fourth on its extraction by long boiling with ether and its precipitation and weighing as  $\text{BPO}_4$ . The following method is a combination of the second and third, designed to permit the determination, most conveniently, of boron in the presence of other common alloying elements. The accuracy of the procedure has not yet been determined.

**Special Solutions Required.**—All solutions must be prepared and kept so that they will be free of  $\text{CO}_2$ .

**Phenolphthalein Indicator Solution.**—Dissolve 1 g of phenolphthalein in 100 ml of neutral ethyl alcohol freshly distilled from  $\text{CaO}$  and add 100 ml of  $\text{CO}_2$ -free water.

*Mannite*.—Use solid reagent. This compound, correctly designated as manitol, has the formula  $C_6H_8(OH)_6$ .

*Standard Sodium Hydroxide Solution, 0.1 N*.—Dissolve 100 g of NaOH in 100 ml of water in a waxed tube. Since the solution must be absolutely free of carbonate, add a few ml of  $Ba(OH)_2$  and let the solution stand several days tightly stoppered or closed with a stopper bearing a  $CO_2$  trap. Carefully draw off 6.5 ml with a calibrated pipette and dilute to 1 liter with freshly boiled cold water. To standardize the solution, use pure boric acid as follows: Fuse the acid in a platinum dish, crush while still warm, and weigh 1.741 g in a weighing bottle. Add to 250 ml of warm freshly boiled water. Cool and dilute to 500 ml, for 0.1 *N* solution, to 1 liter for 0.05 *N* solution.

One ml of 0.1 *N* solution = 0.00108 g of boron.

Standardize the NaOH solution against this solution by direct titration, using the same volumes, etc., as directed in the method. Also, add measured amounts to a boron-free steel solution and analyze by the same procedure used in analyzing the sample.

### Procedure Using Electrolysis Over Mercury Cathode and Calcium Carbonate Separations

#### Solution of the Sample and Separation by Electrolysis

Transfer 1 g of the sample of steel to a 150-ml Erlenmeyer flask equipped with a reflux condenser. Add 15 ml of dilute sulphuric acid (1:4), and let the steel dissolve in the cold, if it will. If not, heat gently until solution is complete. Cool, if necessary, add 5 to 8 drops of 30-per cent  $H_2O_2$  (Perhydrol), and boil for several minutes to oxidize iron, etc. Pour 50 ml of warm water through the condenser to rinse it, disconnect it, and rinse the wall of the flask with a fine jet of water. Neutralize with 1 *N* NaOH solution,  $CO_2$ -free, and acidify with 0.2 ml of  $H_2SO_4$  (sp. gr. 1.84). Transfer to a 250-ml beaker containing about 1 in. of pure mercury, set the beaker in cold water, and electrolyze at 5 amps and 10 volts until the solution is practically free of iron, keeping the temperature below 30° C with ice water, if necessary. During the electrolysis, stir the solution mechanically, if possible; otherwise, keep it agitated by stirring frequently by hand. Decant the solution from the mercury into a small beaker, and treat as directed below.

#### Titration of $H_3BO_3$ : Absence of Al, As, Cb, Ta, Ti, W, V, or Zr

Filter the solution into a 250-ml beaker and wash with water to a total volume of 100 ml. Add 3 to 5 drops of methyl orange and titrate the free  $H_2SO_4$  with 0.05 *N* NaOH to a faint rose color, then dropwise (preferably with 0.01 *N* solution if B is low) to the orange. Back-titrate with 0.05 *N*  $H_2SO_4$ , if desired to fix the end point. Add a few drops of phenolphthalein, take the alkaline reading, and continue

adding the sodium hydroxide solution until the solution begins to show pink. Add 1 g of mannite and titrate to a faint pink. Repeat until the addition of mannite does not cause the color to disappear, and take a reading. Calculate the percentage of boron in the sample.

### **Separation with $\text{CaCO}_3$ and Titration of $\text{H}_3\text{BO}_3$**

Transfer the electrolyzed solution to a round-bottom 600-ml Jena flask, equipped with a reflux condenser, and add 1 g of ferric sulphate, or chloride, and 100 ml of water. Mix and add all at once, twice as much very finely ground pure calcium carbonate as is required to neutralize the acid, and boil the solution under the reflux condenser for 30 minutes to decompose bicarbonates and expel  $\text{CO}_2$ . Add 50 ml of well washed asbestos fiber suspended in hot water and boil 5 minutes longer. Filter through paper in Büchner funnel and wash 8 to 10 times with boiling water. Remove the funnel, and apply the suction direct to the flask to cause low temperature boiling and expel  $\text{CO}_2$  completely.

Cool the solution rapidly to room temperature, add a few drops of phenolphthalein solution, and titrate with 0.05 N NaOH to a pink color. Add 1 g of mannite and add more NaOH to a pink end point. Repeat the addition of mannite and the titration until mannite does not cause the pink color to fade. Subtract the ml of NaOH used in the blank run, using the same amount of ferric sulphate or chloride, and multiply the corrected volume by the boron titer of the NaOH solution. Multiply by 100 and divide by the weight of sample used to find the per cent boron.

### **Method Based Upon the Calcium Carbonate Separation**

The following method, given in brief, is said to give reasonably accurate results for boron in iron and steel. Lacking an authoritative standard steel, we have not been able to determine its accuracy when applied to the determination of boron in steel.

### **Procedure**

Transfer 2 to 3 g of the sample and the same weight of a sample of steel free of boron but otherwise of similar composition to separate round-bottom flasks, and treat each with a mixture composed of 10 ml of  $\text{H}_2\text{O}$ , 10 ml of  $\text{HCl}$ , and 10 ml of  $\text{HNO}_3$ , using no more than is necessary to dissolve the sample and leave a moderate excess. When action of the acid mixture has ceased, cool the flask and contents to room temperature, rinse the neck with a little water, and, while agitating vigorously, add dry finely powdered calcium carbonate,  $\text{CaCO}_3$ , to complete neutralization of the solution. To decompose bicarbonates formed and expel carbon dioxide, add 250 ml of freshly boiled water, attach the flask to a reflux condenser, and boil the mixture for 30

minutes or longer. Introduce about 50 ml of a hot, neutral, water suspension of thoroughly washed asbestos fiber, and continue the boiling for 5 minutes.

Filter the mixture by suction upon a Büchner funnel, and wash the insoluble matter 10 times with boiling hot water. Remove the funnel and apply suction direct to the flask to free the solution entirely of  $\text{CO}_2$ . Cool rapidly to room temperature and proceed with the titration at once.

Titrate both the blank and the sample with 0.1 *N* NaOH and mannite as directed in the last paragraph of the preceding method. From the volume of the 0.1 *N* NaOH solution required to titrate the sample, subtract the number of ml required to titrate the blank. Multiply the difference by the boron titer of the solution, and by 100, and divide by the weight of sample used to find the per cent boron in the sample.

## Determination of Beryllium

Beryllium has been added to steel for experimental purposes without promise that it will prove sufficiently effective in modifying the properties of the metal to justify its cost as an alloying element. Whether or not it already exists in steel in traces is unknown.

With the detailed directions given in the use of the reagents employed for its separation, the following outline of the method employed is sufficient for the present purpose.

### Outline of Procedure

Dissolve 1.0 to 0.5 g of sample, depending upon sensitivity desired, in 15 to 25 ml of  $\text{H}_2\text{SO}_4$  (1:9). Add  $\text{NH}_4\text{OH}$  (1:1) until the precipitate formed just dissolves. Electrolyze with mercury cathode and platinum anode in customary manner until all the iron is removed. Precipitate aluminum and traces of other metals with 8-hydroxyquinoline in acetic acid solution. Filter, wash precipitate, and destroy the organic matter in the filtrate by fuming with sulphuric and nitric acids. Dilute somewhat and make ammoniacal. Beryllium over 0.01 per cent on a 1-g sample causes a white flocculent precipitate which can be filtered and weighed.

*Note.*—A much more sensitive test is made by the use of curcumin as described by Hillebrand and Lundell, "Analysis of Silicate Rocks," page 404, footnote 3, or more fully in the Journal of the American Chemical Society, 50, 393 (1928). This test may be applied in the absence of a precipitate of  $\text{Be}(\text{OH})_2$ .

# Determination of Nitrogen

## Effects of Nitrogen

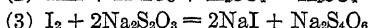
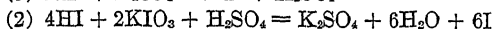
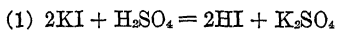
All irons and steels contain nitrogen. The proportion varies between the limits 0.002 to 0.02 per cent in ordinary carbon steels, open-hearth steel containing the least, with Bessemer and electric steels containing somewhat more. Nitrogen forms a nitride with iron, which decomposes at elevated temperatures well below the melting points of iron and steels, which fact accounts for the little nitrogen present in steels in which it has not been introduced through special means. The presence of certain alloying elements increases the nitrogen content somewhat, probably through the formation of more stable compounds than the iron nitride. The effect of nitrogen in such small percentages is negligible. In larger proportions it has a hardening effect, more intense than carbon or any other element commonly added to steel, so it is used to case-harden many articles. Certain operations performed on steel in fabricating or processing result in local concentrations of nitrogen, one example being that of electric welding with bare electrodes. In these special cases, the nitrogen content of the affected parts will be considerably higher than that normally in the steel. The incidental and intentional additions of nitrogen to steel have necessitated an accurate method for its determination, aside from that of knowing the percentage of nitrogen occurring in the metal as produced.

## Methods Available

Only two methods for determining nitrogen have been developed, one known as the vacuum fusion method, and the other as the solution or solution and distillation method, which is also called the Allen method. The vacuum fusion method, though it has been much improved, requires expensive apparatus, an expert operator, and several hours' time for a determination. The solution method has also been improved until it is now as accurate as or more accurate than the vacuum fusion method. The method given below as a standard procedure was developed by coöperative efforts over a period of 7 years by members of this committee, who also acknowledge helpful suggestions by other chemists who have published the results of their investigations. In recognition of this fact, one of the methods recommended for stainless steel is given later.

**Standard Solution and Distillation Method: Digestion in  
Sulphuric and Orthophosphoric Acids, Followed by  
Indirect Titration With KI, KIO<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**

As noted above, most of the nitrogen in steel is present as iron nitride, which reacts with acids to form the ammonium salt of the acid used. The rest of the nitrogen, we believe, is present as iron cyanide, which is insoluble in dilute acids, but was found by W. D. Brown to be convertible to an ammonium salt by long digestion with a mixture of sulphuric and orthophosphoric acid.\* The time necessary for digestion varies with the grade of steel, high-carbon steel, also pig iron, requiring a longer period of digestion than low-carbon steel. Among others, high-silicon steel (4-per cent grade) and high-titanium stainless steels require maximum periods of digestion. The addition of 0.1 to 0.2 g of selenium before the digestion is begun generally shortens the time to about half that required when no selenium is added. To the resulting solution of ammonium salt, NaOH is added, and the ammonia is distilled into an excess of dilute sulphuric acid. The excess acid is then titrated by adding KI and KIO<sub>3</sub>, thus liberating iodine according to reactions 1 and 2, which in turn is absorbed with a slight excess of sodium thiosulphate according to reaction 3.



Starch is then added and the excess sodium thiosulphate is back-titrated with iodine. This roundabout method of titrating was resorted to in order to avoid errors inherent in the color method for nitrogen and in the direct titration of extremely dilute solutions of acid and alkali with indicators available for use in the presence of ammonium salts. However, except for very small proportions of nitrogen, the acid-alkali titration, using methyl red as an indicator, is entirely satisfactory.

**Determination of Nitrogen in Pig Iron and Steel**

**Apparatus**

The distilling apparatus for ammonia is shown in Fig. 16.

A 300-ml round-bottom Pyrex digestion flask is used for dissolving and digesting the sample. The flask is heated and the digestion effected upon a Kjeldahl electric digestion apparatus equipped with rheostat for regulating the heat. For distilling the ammonia produced in the treatment following the digestion, a Maharg still is modified by grinding a separatory funnel into the neck of the distilling flask and placing an alkali trap in the side arm. A modified Volhard

\* Trials have shown that the use of perchloric acid, either alone or mixed with sulphuric acid or with sulphuric and phosphoric acids, gives low results.

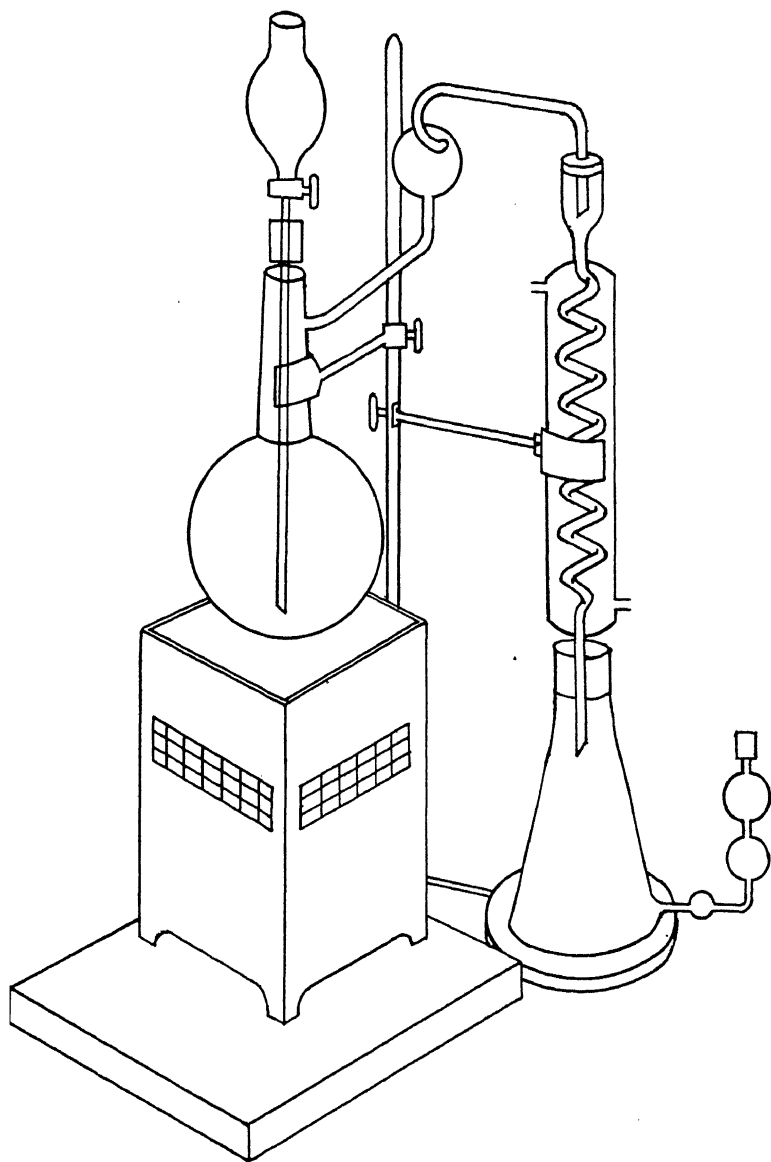


FIGURE 16. Assembly of apparatus for distilling the ammonia formed. Note: The refractory ring supplied with the heater is removed, and the flask itself is raised several inches above the heater to prevent bumping.



nitrogen flask is used to receive the condensate from the Maharg still. The distilling flask is heated with a 550-watt electric heater equipped with a rheostat. The standard solutions are measured in 10-ml burettes.

To prevent bumping during the long boiling with sulphuric and phosphoric acids, the refractory ring is removed from the heater and the flask is raised several inches above the heater.

### Special Reagents and Solutions Required

**Ammonia-free Water.\***—Water, free from ammonia and alkali, is prepared in a still consisting of a 12-liter glass flask connected to a block tin condenser by means of block tin and glass (Fig. 17). Rubber connections are thus avoided. The flask is filled with distilled water,

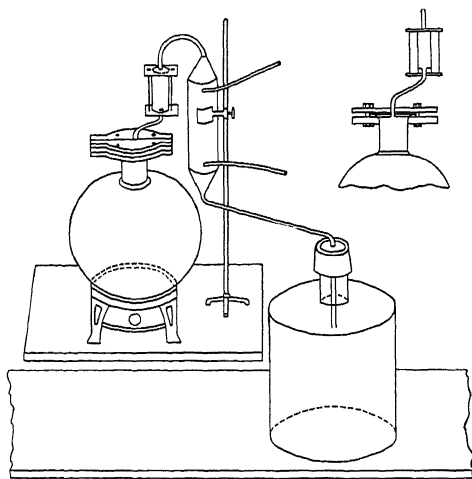


FIGURE 17. Apparatus for the preparation of ammonia-free water.

and a small amount of Devarda's alloy (50 parts Al, 45 parts Cu, and 5 parts Zn) is added. Ten ml of sodium hydroxide solution (sp. gr. 1.27) are added, the solution is digested below the boiling point for 12 to 16 hours, and boiled till the volume is reduced by 500 ml. The flask is connected to the condenser and heated, and 100 ml of the distillate are collected and tested with Nessler's reagent. The distillation is continued, and this test is repeated until no indication of ammonia is found in 2 succeeding tests. The ammonia-free water is then collected in a large glass bottle. By this treatment, nitrates and nitrites which might give high results are eliminated.

**Sulphuric Acid (sp. gr. 1.23).**—Nine hundred ml of sulphuric acid (sp. gr. 1.84) are added to 3 liters of ammonia-free water (not neces-

\* Alkaline ammonium-free water is prepared by almost filling a 12-liter flask with distilled water, adding 5 g of NaOH and 2 g of Devarda's alloy, digesting 12 to 16 hours, and rapidly boiling down to between 9 and 10 liters.

sarily alkaline-free) in a flask. The solution is stirred and cooled under running water. When the solution is cold, the sp. gr. should be 1.23.

**Sulphuric-Phosphoric Acid Mixture.**—To 68 ml of diluted  $\text{H}_2\text{SO}_4$  (sp. gr. 1.23), 5 ml of phosphoric acid (85-per cent) are added.

**Sulphuric Acid, 100-per cent.**—One hundred fifty ml of low-nitrogen 15-per cent fuming sulphuric acid are added to 200 ml of concentrated sulphuric acid (sp. gr. 1.84).

**Phosphoric Acid, 85-per cent.**—A grade of C. P. acid low in nitrogen is used.

In order to obtain these acids uncontaminated with nitrogen compounds, it is necessary to take them from bottles or carboys not previously opened, and thereafter avoid exposing them to the air.

**Sodium Hydroxide (Sp. Gr. 1.27).**—Three liters of distilled water are placed in a 6-liter flask and the level marked with a pencil. In it, 1000 g of sodium hydroxide (sticks, electrolytic) are dissolved, the flask being shaken to mix. A slight excess of barium hydroxide is then added to precipitate any carbonate present. A few grams of Devarda's alloy are added to convert any nitrates to ammonia, followed by 500 ml of distilled water. The solution is digested for a few hours before boiling, and then boiled until but 3 liters remain. The solution is allowed to cool and stand until the precipitate has settled. It is then decanted into a glass bottle and diluted with ammonia-free water to a specific gravity of 1.27.

**Potassium Iodide Solution (2-per cent).**—Ten grams of alkali-free potassium iodide are dissolved in 500 ml of distilled water which has been boiled until free from carbon dioxide.

**Potassium Iodate Solution (0.3-per cent).**—One and a half grams of alkali free potassium iodate are dissolved in 500 ml of carbon dioxide-free distilled water.

**Starch Solution.**—This solution must contain no alkali. Starch prepared in the following manner meets this requirement and keeps at least several months. Ten milligrams of mercuric iodide are rubbed to a fine powder in a mortar. With it are ground 2.5 grams of wheat starch. The mixture is transferred to a liter beaker which is then filled with boiling distilled water. The solution is stirred and allowed to stand 12 to 15 hours, when the clear portion is poured into a bottle. Ten ml are used for each 100 ml of solution to be titrated.

**Standard Sulphuric Acid (0.01 N).**—Two and two-tenths ml of dilute sulphuric acid (1:1) are diluted to 3 liters and after being well mixed the solution is titrated with standard sodium hydroxide. It should be between 0.0095 *N* and 0.0105 *N* but its exact normality need not be known.

**Standard Sodium Thiosulphate (0.013 N).**—Nine and seven-tenths grams of sodium thiosulphate are dissolved in 3 liters of distilled water. The solution is kept in a cool dark place.

**Standard Iodine Solution (0.01 N).**—Seven and a half grams of potassium iodide are dissolved in 15 ml of distilled water. Three and eighty-one hundredths (3.81) grams of resublimed iodine are weighed into a weighing bottle and quickly shaken into a stoppered liter flask. The weighing bottle is rinsed into the flask with the potassium iodide solution and the flask shaken until all the iodine is dissolved. The flask is filled up to the mark with distilled water and poured into the stock bottle. Two more liters of distilled water are added and the solution is well mixed and kept in a cool dark place.

The method for standardizing the iodine and sodium thiosulphate solutions is given after the procedure, below.

### Blank

A blank determination carried through all steps of the procedure must be made on each lot of sulphuric and phosphoric acids made up. With care in protecting the solutions from the atmosphere of the laboratory one blank on each lot is sufficient. However, a blank should be run whenever there is any doubt as to chance exposure of the reagents to any condition that may result in contamination with nitrogen in any form.

### Procedure

**Solution and Digestion of the Sample.**—For a nitrogen content up to 0.025 per cent in plain steel and pig iron, transfer 5 g of sample to a 300-ml Kjeldahl digestion flask. For metals containing a high percentage of alloying elements, use a 2.5 g sample; otherwise, excessive bumping will ensue in the subsequent distillation. Add 0.2 g of elementary selenium, 68 ml of sulphuric acid (sp. gr. 1.23), and 5 ml of phosphoric acid (85-per cent), and hasten solution by heating below the boiling point. For high-silicon steels and others that dissolve slowly, add 50 ml of water. When dissolved, boil vigorously to remove the water rapidly and digest the mass of ferrous sulphate until it is thick and pasty. Rinse the wall of the flask with 10 ml of 100-per cent sulphuric acid, and digest the mass for 2 to 8 hours over a 550-watt electric heating unit adjusted to a maximum temperature whereby the mass is still fluid at the end of the digestion. Regulate the exact time of digestion according to the kind and grade of material as indicated in the preliminary discussion of the method. Cool the flask slightly and add 100 ml of ammonia-free water. If the sample is high in silicon, add  $\frac{1}{2}$  g of potassium fluoride for each per cent of silicon present in the 5-g sample. Boil the solution briskly for a few minutes and then gently until most of the ferric sulphate is in solution. With alloy steels, make no attempt to dissolve all the

salts, for such a prolongation of the boiling is unnecessary. Then, remove the flask from the heat and cool.

Fit a No. 7 rubber stopper on the discharge end of the condenser; and clamp the condenser, distilling flask, and electric heater to a heavy ring stand. To assure even heating of the flask and avoid bumping, remove the refractory ring from the heater and lower it so that the lowest part of the bottom of the flask is slightly above the top rim of the heater. Leave enough room under the discharge end of the condenser to accommodate either a 50-ml graduate or the nitrogen flask. Connect the condenser to a water tap in the usual manner and fill the seal half full with clean mercury.

By means of a funnel, pour 150 ml of sodium hydroxide solution (sp. gr. 1.27) into the distilling flask, rinse the funnel with 200 ml of ammonia-free water, and carefully remove it. Moisten the ground surface of the stopper on the separatory funnel with ammonia-free water, and place the funnel in the flask. Rinse the funnel with 25 ml of ammonia-free water, and turn the stopcock so that it fits loosely. Use care that no alkali comes in contact with stopper and stopcock. Turn the current on the heater, and distill 50 ml of water into a graduate to insure that still and contents are ammonia-free. Shut off the current, and uncouple the distilling flask from the condenser, cool under running water for one minute, and reconnect it. Connect the nitrogen flask, into which exactly 10 ml of standard sulphuric acid have been measured from a 10-ml burette, with the condenser, and draw a plate support up to hold the flask. Close the seal of the flask by tilting the ring stand, and pour the cooled sample through the separatory funnel. Rinse the digestion flask a few times with 30 to 50 ml of ammonia-free water, bringing the volume to about 500 ml. Close the stopcock, and agitate the distilling flask by gently moving the ring stand. Heat, and distill 100 ml into the nitrogen flask, estimating the volume by marks made beforehand on the flask to show the capacity of 110 ml for various levels of distillate in the receiving flask.

Remove the receiving flask, add 5 ml of 2-per cent potassium iodide solution and 5 ml of 0.3-per cent potassium iodate solution from a graduate, and follow immediately by exactly 10 ml of standard thiosulphate solution measured from a 10-ml burette. Stir the contents of the flask well by rotating, and allow it to stand for 5 minutes. Add 10 ml of starch solution, and titrate the solution to a blue end point with standard iodine from a 10-ml burette. From the readings taken and the values obtained as directed in the next two paragraphs, calculate the per cent nitrogen in the sample.

**Daily Titration Blank.**—A blank must be run daily on the standard thiosulphate and standard sulphuric acid. Add exactly ten ml of standard sulphuric acid from the burette, 5 ml of 2-per cent potassium

iodide, and 5 ml of 0.3-per cent potassium iodate to a 300-ml Erlenmeyer flask, and follow immediately by exactly 10 ml of standard thiosulphate from the burette. Rotate the flask to stir the solution, allow to stand for 5 minutes, and titrate with standard iodine after the addition of 10 ml starch solution. This is the titration blank. It must be over 1 ml else the standard thiosulphate is too weak; in which case, it must be renewed.

**Method for Standardizing the Iodine and Sodium Thiosulphate Solutions.**—The iodine solution is standardized as follows: Transfer to a 400-ml beaker, 0.0817 gram of acid potassium phthalate (Standard No. 84, National Bureau of Standards) and dissolve in 20 ml of the 2-per cent potassium iodide solution. Add 20 ml of 0.3-per cent potassium iodate solution, and follow immediately by exactly 40 ml of standard sodium thiosulphate solution from a burette. Allow the beaker to stand for 1 hour with occasional stirring and titrate with standard iodine solution after the addition of 10 ml of starch solution.

Also compare the standard thiosulphate and the standard iodine. Add to a 400-ml beaker 20 ml of 2-per cent potassium iodide solution, 20 ml of 0.3-per cent potassium iodate, and 40 ml of the standard sodium thiosulphate solution, and allow the mixture to stand for one hour. Then, titrate with the standard iodine solution after the addition of 10 ml starch solution.

**Calculation.**—The difference between these two titrations represents the standard iodine solution equivalent to the acid potassium phthalate used. The weight of this salt used (0.0817 g) is equivalent to 40 ml of 0.01 *N* solution. Therefore, the normality of the iodine is ( $40 \times 0.01$ ) divided by the number of ml of iodine equivalent to the acid potassium phthalate. The weight of nitrogen equivalent to 1 ml of the standard iodine, and expressed as fraction of a gram, is found by multiplying the normality by 0.014008.

**Example:**

Iodine used by 40 ml thiosulphate .....	51.82 ml
Iodine used by phthalate and thiosulphate.....	12.94 ml
Iodine equivalent to 0.0817 g phthalate .....	38.88 ml
Strength of iodine ( $40 \times 0.01$ ) divided by 38.88.....	0.010288 <i>N</i>
Strength of iodine in terms of nitrogen $0.010288 \times 0.014008$ .....	0.0001441 g

The number of ml of standard iodine used on the reagent blank, minus the number of ml of standard iodine used on the titration blank, multiplied by the nitrogen factor of the standard iodine, gives the grams of nitrogen in the reagents. This figure is constant until acids for solution and digestion are changed, when it must be redetermined.

The number of ml of standard iodine used in the determination, minus the number of ml of standard iodine used on the titration blank, multiplied by the nitrogen factor, gives the grams of nitrogen

found in the determination. This figure, minus the weight of nitrogen found in the blank, multiplied by 100, and divided by the weight of the sample gives the per cent of nitrogen in the sample.

**Example:**

Iodine used in reagents blank .....	2.63 ml
Iodine used in titration blank .....	2.02 ml
Iodine equivalent to nitrogen in reagents .....	0.61 ml
Nitrogen factor of standard iodine, 0.0001441 .....	
Nitrogen in reagents, $0.61 \times 0.0001441$ .....	0.0000879 g
Iodine used in determination .....	5.43 ml
Iodine used in titration blank .....	2.02 ml
Iodine equivalent to nitrogen in determination .....	3.41 ml
Nitrogen factor of standard iodine, 0.0001441 .....	
Nitrogen in determination, $3.41 \times 0.0001441$ .....	0.0004914 g
Nitrogen in reagents .....	0.0000879 g
Nitrogen in 5-g sample .....	0.0004035 g
Nitrogen in material .....	0.00807 per cent

### Modified Method Employing Acid-Alkali Titration With Methyl Red as Indicator

**Special Solutions Required**

With two exceptions the solutions are the same as those employed in the preceding method. Instead of the standard iodine and thio-sulphate solutions used for titrating, the following are used:

**Standard Sulphuric Acid (0.02 N).**—Add 1.2 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) to 1 liter of distilled water.

Titrate against the standard NaOH solution and adjust the volume to make 1 ml of the acid equivalent to 1 ml of the NaOH solution.

**Standard NaOH Solution (0.02 N).**—Dilute 135 ml of 0.148 N or 200 ml of 0.10 N NaOH solution to 1 liter with cold recently boiled distilled water.

**Example:**

Sodium hydroxide used for phthalate indicator and water = 25.42 ml	
Sodium hydroxide used for indicator and water .....	= .12
Sodium hydroxide used for phthalate .....	= 25.30
25.00	
25.30	
$\frac{25.00}{25.30} \times 0.02 = 0.01976 = \text{Normality of NaOH}$	
$0.01976 \times 0.014008 = 0.0002768 \text{ g N per ml}$	
$= 0.02768 \text{ per cent N on 1 g sample}$	
$= 0.01384 \text{ per cent N on 2 g sample}$	
25.00	
25.30	
$\frac{25.00}{25.30} \times 0.02802 = 0.02768 = \text{per cent nitrogen equal to 1 ml of the}$	
solution when a 1-g sample is taken.	

**Methyl Red Indicator**

Methyl Red .....	0.1 g
NaOH (0.1482 N) .....	3.5 ml
$\text{H}_2\text{O}$ .....	100 ml

Standardize this solution, and repeat the standardization at frequent intervals, as follows:

Weigh into a clean 400-ml beaker 0.1020 g of Bureau of Standards acid potassium phthalate. Add about 50 ml of cold, boiled distilled water, and 2 or 3 drops of phenolphthalein indicator. Titrate with the sodium hydroxide to the first permanent faint pink color, being sure that the phthalate is all dissolved before the end of the titration. Titrate the same amount of water and indicator to the same color as a blank. Calculate values as illustrated in the example on page 295.

### Procedure

**Caution.**—All flasks, graduates, etc., used on the receiving end of the condenser must be neutral. All other glassware must be rinsed with nitrogen-free water before using.

**Weight of Sample.**—For a nitrogen content up to 0.05 per cent in plain steel or pig iron use a 5-g sample. For higher nitrogen content in these materials 1- or 2-g samples may be used. On high-chromium (18 to 25 per cent) steels, 1- or 2-g samples should be used. On account of the formation of insoluble compounds which cause bumping, not more than 2 g should be used. For the same reason not more than 0.5 to 0.7 g of ferrochromium should be taken.

Transfer the sample to a 300-ml Kjeldahl digestion flask. Add 0.2 g selenium and sulphuric-phosphoric acid mixture as follows:

For 5-g sample .....	73 ml
For 2-g sample .....	50 ml
For 1-g or less .....	40 ml

Heat to dissolve and evaporate rapidly until fumes are distinctly visible. Without cooling, rinse the neck of the flask with 10 ml of 100-per cent sulphuric acid. Digest for 2 to 4 hours, regulating the heater so that there is gentle boiling in the flask and a slight escape of fumes from the outlet. Cool somewhat. Carefully add 100 ml of nitrogen-free water. Shake, boil several minutes, and cool again.

The salts from plain steel should all dissolve. Chrome salts will not dissolve but the heating should be continued until all or nearly all of the iron salts are in solution.

In the meantime carefully rinse the distillation flask, condenser, and receiving flask. Through a special funnel, add to the distillation flask sodium hydroxide solution (sp. gr. 1.27) as follows, being careful to prevent any of the solution from coming in contact with the neck of the flask.

150 ml NaOH if 73 ml of acid were used to dissolve the sample
135 ml NaOH if 50 ml of acid were used to dissolve the sample
125 ml NaOH if 40 ml of acid were used to dissolve the sample

Rinse the funnel and neck of the flask with 100 ml of nitrogen-free water. Rinse the special glass stopper with a few ml of nitrogen-free water, put it in place, and make it tight with a twisting motion.

Into the receiving flask, carefully transfer enough standard 0.02 *N* sulphuric acid to absorb the ammonia and provide an excess, 10 ml of the acid being sufficient for about 0.27 per cent nitrogen on a 1-g sample or 0.13 per cent on a 2-g sample.

Tilt the flask to put some acid in the seal and connect it to the condenser. See that all connections and supports are in good condition and that the proper flow of water is established in the condenser. Rinse the other special funnel with nitrogen-free water and through it pour the contents of the digestion flask, using 70 ml of nitrogen-free water to rinse this flask. Finally lubricate the glass stopcock with a few ml of nitrogen-free distilled water and put it in loosely.

Place the heater so that there is about  $\frac{1}{8}$ - to  $\frac{3}{4}$ -inch clearance between the flask and the heating element, turn on the full current, and heat the flask thus until 100 ml of distillate have been driven over as shown by a mark on the receiver.

Disconnect the heater and remove it at once. Disconnect the receiver, add immediately 3 drops of methyl red indicator, and titrate with standard sodium hydroxide solution to a full yellow end point.

**Reagent Blank.**—Make a blank determination on the reagents each time new acids are made up, and as frequently between these periods as may appear necessary. Conduct these blank runs in exactly the same way as a regular determination.

**Daily Titration Blank.**—Add to one of the receiving flasks about 50 ml of ordinary distilled water and the same amount of 0.02 acid as was used in the test. Titrate to the same end point as that established for the determination. Determine this blank each day for the different portions of this acid used.

**Calculation of Results.**—From the results of the analysis and blank runs, calculate the per cent nitrogen in the sample as illustrated by the following example.

Titration blank, standard NaOH solution to titrate 0.02 <i>N</i>		
H <sub>2</sub> SO <sub>4</sub> used .....	11.00 ml	
NaOH used in back-titration of reagent blank .....	10.80 ml	
NaOH used in back-titration of sample blank .....	3.45 ml	

Assuming that a 1-g sample was used and the normality of the NaOH is exactly 0.02, 1 ml is equivalent to 0.028 per cent on a 1-g sample. Therefore,

$$\begin{aligned}
 11.00 & - 10.80 = 0.20 \text{ ml} = \text{reagent blank} \\
 11.00 & - 0.20 = 10.80 \text{ ml} = \text{net blank} \\
 10.80 & - 3.45 = 7.35 \text{ ml NaOH equivalent to the nitrogen in the} \\
 & \quad \text{sample.} \\
 0.0280 \times 7.35 & = 0.206 \text{ per cent nitrogen in the sample.}
 \end{aligned}$$



## Methods for the Determination of Nitrogen in Stainless Steel

### Solution of the Sample in HCl With Digestion of Insoluble Residue in $\text{H}_2\text{SO}_4$ : Absorption of $\text{NH}_3$ in HCl and Titration of Excess with NaOH

This method, the procedure for which is briefly outlined below, has been employed by Thomas R. Cunningham to obtain results that compare favorably with those obtained by the preceding method. In the absence of vanadium, titanium, columbium, or other elements forming nitrides insoluble in hydrochloric acid, it provides a simple means for the estimation of nitrogen in steel.

**Special Reagents Required.**—*Ammonia-free water.*—Add 200 g of KOH and 8 g of  $\text{KMnO}_4$  to 1100 ml of distilled water, and boil the mixture down to a volume of approximately 1000 ml. Add 1 part of this solution to 10 parts of the water to be purified, and distill through a block tin condenser until a test on 100 ml of the distillate, containing 2 drops of the indicator solution, does not require more than 2 drops of 0.01 N solution of HCl.

*Indicator Solution.*—Dissolve 1 g of sodium alizarine sulphonate in 100 ml of freshly distilled water and keep in a glass-stoppered bottle.

**Solution of the Sample.**—Treat the sample as follows, running a blank on reagents through all steps of the analysis. Transfer 5 g of the sample to a 300-ml platinum dish provided with a tight fitting cover. Add 35 ml of ammonia-free water and 35 ml of HCl taken from a bottle that has not been opened before, adding the acid gradually if the reaction is energetic. When the violent action has ceased, add 3 ml of HF (48-per cent) from a newly opened bottle, and heat on a water bath until solution of the metal is complete.

If the metal dissolves completely in the dilute HCl, the HF may be omitted and the sample dissolved in a 150-ml covered beaker.

While the sample is dissolving, add, to a Kjeldahl flask, 100 ml of a solution containing 1000 g of NaOH per liter, several small pieces of mossy zinc, about 400 ml of water, and 20 g of tartaric acid, the last being added to help hold iron and chromium in solution. Using a condenser tube of block tin, distill over 200 ml from this mixture and discard the distillate. Then, let the remainder of the alkaline solution in the flask cool to room temperature.

Remove the platinum dish or beaker from the water bath and permit it to cool. If the steel contains vanadium, titanium, columbium, or other elements whose nitride is insoluble in HCl, filter the solution through a well washed 9-cm paper and wash with a 1-per cent solution of HCl which has not been exposed to nitrogen-bearing fumes. Reserve the filter and contents for treatment as directed later.

Transfer the filtrate or the solution of the sample, if it was not filtered, to the Kjeldahl flask containing the prepared alkaline solu-

tion, rinsing the dish or beaker with four 50-ml portions of ammonia-free water. Connect the Kjeldahl flask to the condenser, and the delivery tube of the condenser to an absorption flask containing a carefully measured volume of 25 to 50 ml of 0.02 *N* solution of HCl, the quantity of the acid solution being varied according to the nitrogen present. Boil the contents of the Kjeldahl flask until 200 ml of condensate have been collected in the absorption flask. Disconnect the flask from the condenser, add 2 drops of a 1-per cent water solution of sodium alizarine sulphonate as an indicator, and titrate the excess of acid with 0.02 *N* solution of NaOH, taking as the end point the complete disappearance of the clear yellowish-green color or the first indication of a brown color.

Subtract the ml of 0.02 *N* NaOH solution used from the ml of 0.02 *N* HCl added to the flask to find the ml of the latter neutralized by the ammonia formed.

Titrate the blank to the same end point, and correct the volume of standard acid neutralized by the ammonia or the calculated nitrogen result accordingly. To find the per cent nitrogen, multiply the corrected number of ml of 0.02 *N* HCl neutralized by the ammonia formed by  $0.00028 \times 100$ , and divide by the weight of sample used.

If sodium alizarine sulphonate is not available, make the titrations potentiometrically, using a pH meter with glass electrode.

If the steel contained vanadium, titanium, columbium, etc., making it necessary to treat the acid-insoluble residue, correct the result obtained above for the nitrogen found in the residue by treating it, along with a blank, as follows:

Transfer the paper and acid insoluble residue to a 500-ml Kjeldahl flask, and add 10 g of potassium sulphate, 1 g of copper sulphate, and 20 ml of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84). Using care to see that the flask is not heated above the surface of the liquid, heat the flask gradually and maintain the temperature below the boiling point of the acid until the frothing ceases. Continue the heating and boil the contents of the flask for 15 to 20 minutes after the solution has become colorless. Cool to room temperature, add 200 to 250 ml of ammonia-free water, connect the flask to the condenser and introduce 100 ml of a 10-per cent solution of NaOH. Heat to boiling and complete the determination of the acid-insoluble nitrogen as directed above for the acid-soluble nitrogen. Deduct the nitrogen found in the blank and add the difference to the nitrogen obtained in the filtrate to give the total nitrogen present in the steel.

# Determination of Antimony (Copper and Molybdenum)

Antimony in proportions exceeding 0.30 per cent makes steel "hot short" and extremely difficult, if not impossible, to roll. In small percentages, say, under 0.030 per cent, its effects do not appear to be harmful in ordinary grades of steel, nor can it be said that any beneficial effect has been noticed. Therefore, antimony is not intentionally added to steel and the probability of its presence is remote. On this account, its determination is seldom requested, but since it may be accidentally introduced through the scrap, a method for its determination is advisable. The following procedure, based largely upon the work of Sherrer (see Bureau of Standards, Research Papers 415 and 871), is intended to provide a method for future use as may be required.

## Standard Procedure

### Solution of the Sample

**Steels and Irons Soluble in Nitric Acid.**—Transfer 10 g of sample to a 600-ml beaker, and dissolve with a suitable acid as follows: For steels that can be decomposed with nitric acid, dissolve the sample with 250 ml of dilute  $\text{HNO}_3$  (1:4), heating gently till decomposition is complete. Boil 5 minutes, and add a slight excess (3 to 5 ml) of a saturated solution of  $\text{KMnO}_4$ . Dissolve the brown oxides of manganese by adding sulphurous acid cautiously and boil off the excess.

If tungsten is present, let the solution stand overnight, decant the clear liquid, add 40 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) to the liquid and residue in the beaker, and boil down to fumes. Add 10 ml of  $\text{HNO}_3$  and fume again. Dilute to 100 ml, add a small excess of  $\text{NH}_4\text{OH}$  and 10 g of tartaric acid. Acidify, filter, neutralize the filtrate, and add it to the clear decanted solution. Cool the combined solutions and treat with  $\text{H}_2\text{S}$  as directed for the precipitation of the sulphides.

In the absence of tungsten, filter the nitric acid solution and reserve the filtrate. Transfer the paper to a 500-ml Erlenmeyer flask, add 10 ml  $\text{H}_2\text{SO}_4$  and 25 ml of  $\text{HNO}_3$ , heat gently, and boil down just to fumes. If the solution is still discolored with carbonaceous matter, repeat the treatment with  $\text{HNO}_3$ . Avoid fuming strongly, if chromium is present. Dilute to 100 ml, add 10 g tartaric acid, boil, filter, if necessary, neutralize with  $\text{NH}_4\text{OH}$ , and add to the reserved filtrate. Treat the combined solutions as directed below for the precipitation with  $\text{H}_2\text{S}$ .

**Steels and Irons Not Soluble in Nitric Acid.**—To decompose steels not attacked by nitric acid, transfer the sample (10 g) to a 600-ml beaker or 500-ml Erlenmeyer flask, add 10 g of  $\text{NaClO}_3$  or  $\text{KClO}_3$ , and dissolve slowly by adding 50 to 75 ml  $\text{HCl}$  in small portions or 40 to 50 ml of dilute  $\text{H}_2\text{SO}_4$  (1:4) and regulating the temperature as required. If a residue remains, separate it by filtering the solution and treating the residue as described above. If  $\text{HCl}$  is used to dissolve the steel, add 20 ml of dilute  $\text{H}_2\text{SO}_4$  (1:4). Finally, boil down the solution, or the combined solutions, just to fumes to decompose the chlorate, and drive off any excess of chloric acid. Cool and treat the solution as described below.

### Precipitation with $\text{H}_2\text{S}$

Dilute the cold solution to 550 ml, and pass a rapid stream of  $\text{H}_2\text{S}$  for 40 minutes. To prevent formation of sulphur, reduce by adding  $\text{SO}_2$ , but since the S does not interfere, omit this step unless it is desired to observe the precipitate formed. Let the beaker stand for 1 hour, filter, and wash with a 5-per cent solution of  $(\text{NH}_4)_2\text{SO}_4$  saturated with  $\text{H}_2\text{S}$ . Transfer the paper and precipitate of arsenic, antimony, tin, copper, and molybdenum sulphides, plus sulphur, etc., to a 500-ml beaker, and treat with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  as described above for the first residue, in the presence or absence of tungsten, but fume strongly. Cool and dilute to 100 ml. Boil 5 to 10 minutes, add 15 ml of  $\text{HCl}$ , and filter, if necessary to remove sulphur and graphite, and wash the filter with water. If copper or molybdenum or both are present, separate them as directed below, which step may be omitted if neither is present.

### Ammonia Separation of Copper and Molybdenum

Add about 0.1 mg of ferric chloride or sulphate to the clear solution, dilute to 200 ml, heat to boiling, and stir in ammonia until there is an excess of 3 to 5 ml. Boil one minute, filter, and wash 3 times with dilute ammonia (2-per cent) and 2 or 3 times with water. Reserve the filtrate for the estimation of copper and molybdenum by color methods, if desired, and, with a hot solution of 80 ml of  $\text{HCl}$  in 100 ml of water, dissolve the precipitate of ferric hydroxide carrying the arsenic, antimony, and tin, into a 500-ml Erlenmeyer flask, using no more of the solution than is necessary.

### Separation of Arsenic

To separate arsenic, which interferes with the subsequent titration of antimony, proceed by one of the following methods.

1. In the absence of arsenic and tin, cool the solution in running water, and pass a stream of  $\text{H}_2\text{S}$  through it for 40 minutes. Filter and wash with dilute  $\text{HCl}$  (8:10). Reserve the filtrate and washings

for antimony, and treat the precipitate to verify presence or absence of arsenic, if desired.

2. Add 15 g of ferrous sulphate to the flask, displace the air with  $\text{CO}_2$ , and distill off the arsenic trichloride, which boils at  $130^\circ \text{C}$ , as in the determination of arsenic, making sure the temperature of the solution does not exceed  $170^\circ \text{C}$  to make a sharp separation from antimony trichloride which boils at  $220.2^\circ \text{C}$ .

### Reprecipitation and Determination of Antimony

With Sherrer's distilling apparatus, antimony may be distilled after the arsenic by raising the temperature finally to  $165^\circ \text{C}$ , but for ordinary work the following procedure is satisfactory.

As large proportions of iron decrease the accuracy of the determination of antimony, separate the latter element as follows: To the strongly acid solution, add ammonia until the solution is alkaline to litmus. Then, add 5 ml of  $\text{HCl}$  for each 100 ml of solution and pass  $\text{H}_2\text{S}$  through it for 20 minutes. Let the precipitate settle for 30 minutes, and wash 6 to 8 times with dilute  $\text{H}_2\text{SO}_4$  (3-per cent) saturated with  $\text{H}_2\text{S}$ . Treat the filter and precipitate by one of the following methods, the first being preferable.

(1) Transfer the filter paper and contents to a 500-ml Erlenmeyer flask, add 25 ml of  $\text{HNO}_3$  and 10 ml of  $\text{H}_2\text{SO}_4$ , and evaporate to fumes. If the solution is not clear of organic or carbonaceous matter, add  $\text{HNO}_3$  again, and evaporate to fumes, repeating these operations as often as necessary. Finally, add 250 ml of water, 25 ml of  $\text{HCl}$ , and 10 ml of a freshly prepared saturated solution of  $\text{SO}_2$ , and boil 15 minutes. Cool to  $10^\circ \text{C}$  and titrate as directed below.

(2) Transfer the paper and precipitate to a Kjeldahl flask, add 10 ml of  $\text{H}_2\text{SO}_4$  and 5 g of  $\text{K}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4$ , and digest (1 to 2 hours) until organic matter is destroyed. Cool, add 250 ml of water and 25 ml of  $\text{HCl}$ , and boil 3 to 5 minutes.

Cool to  $10^\circ \text{C}$ , and titrate rapidly with 0.05 *N*  $\text{KMnO}_4$  solution to a pink color persisting for at least 10 seconds. Subtract the blank for a blank run, multiply by the antimony titer of the  $\text{KMnO}_4$ , and by 10 to find the per cent Sb in the sample. Theoretically, 1 ml of 0.05  $\text{KMnO}_4$  solution = 0.003045 g of Sb, but this titer is used only for very small amounts on account of the large blank.

The  $\text{KMnO}_4$  solution is standardized either by a parallel run with metallic antimony or by use of a standard steel.

# Determination of Zinc

## Occurrence and Methods Available

Zinc is not used as an alloying element in steel, and it is, therefore, not a likely constituent, because it has a low boiling point ( $906^{\circ}\text{C}$ ) and is readily and easily oxidized. However, it may occasionally be introduced accidentally through scrap or alloy additions, and this possibility as well as its use as a coating may be the cause of demands for its determination occasionally. The percentage is usually small, and the methods for its quantitative separation from the large proportion of iron and varying proportions of other elements present are limited to the basic acetate, barium carbonate, ether, and hydrogen sulphide separations, with the first two unsuited to the separation of large amounts of iron. In separating iron with ether, a small percentage of the zinc accompanies the iron, and a double separation is necessary in very exacting work. In the first method below (contributed by Mr. W. F. Muehlberg, December 31, 1934), the initial separation is made with hydrogen sulphide, and satisfactory results have been obtained in the experimental analysis of carbon steels in which 0.005 g of zinc was recovered from 10 g of Bessemer steel with reasonable accuracy.

In making an analysis of steel for zinc, it is important to use zinc-free glassware and avoid entirely the use of rubber as stoppers or policemen.

## Procedure Making the Initial Separation as Sulphide

### Solution of Sample

Transfer 10 g of the sample to a 500-ml Erlenmeyer flask, add 110 ml of dilute  $\text{H}_2\text{SO}_4$  (1:9), and heat to boiling. When solution of the steel is complete, filter the solution rapidly, wash the filter 3 or 4 times with hot water, and discard the black residue of carbon, copper sulphide, molybdenum sulphide, etc. Dilute to 250 ml, add from a burette an 8-per cent solution of sodium carbonate until a slight precipitate forms and remains after vigorous stirring. While stirring constantly, add dilute  $\text{H}_2\text{SO}_4$  (1:9) drop by drop until the precipitate just dissolves, which operation, if carefully carried out, will adjust the acidity to a value between pH 4 and pH 2 (0.0001  $N$  to 0.01  $N$ ).

### Precipitation of Zinc

Cool the solution in running water and pass  $\text{H}_2\text{S}$  at a rapid rate through the solution for 20 to 30 minutes. To obtain complete pre-

cipitation of zinc and facilitate filtering, add 5 to 6 mg of pure copper sulphate crystals and stir with the  $\text{H}_2\text{S}$  delivery tube until the copper sulphate is dissolved. Add a little paper pulp, and allow the precipitate to settle completely. Filter and wash with dilute  $\text{H}_2\text{SO}_4$  (1:99) saturated with  $\text{H}_2\text{S}$ . Reserve the precipitate of copper and zinc sulphides, which will also be accompanied by a little iron sulphide and any As, Mo, Sb, or Sn present.

### Separation of Zinc as Sulphide

Incinerate the paper containing the mixture of sulphides, ignite gently, cool, and transfer the oxides to a 100-ml beaker. Add  $\text{HCl}$ , a very little at a time, and heat until the oxides have been dissolved with a minimum amount of the acid. Add 5 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) and evaporate to fumes. Cool, dilute to 35 to 40 ml, and pass  $\text{H}_2\text{S}$  until the sulphides of copper, molybdenum, arsenic, antimony, and tin have coagulated. Filter and wash with cold dilute  $\text{H}_2\text{SO}_4$  (1:99) saturated with  $\text{H}_2\text{S}$ . Boil the filtrate and washings until  $\text{H}_2\text{S}$  has been expelled, and cool.

### Final Separation of Zinc

Add 3 or 4 drops of methyl orange and neutralize the solution with dilute ammonia. After adjustment of the solution to the neutral point, add 10 ml of 0.1  $N$   $\text{H}_2\text{SO}_4$  and dilute to 100 ml to give an 0.01  $N$  solution or a pH of 2 to 3. Cool the solution in running water and pass a rapid stream of  $\text{H}_2\text{S}$  through the solution for 25 minutes. Permit the precipitate of zinc sulphide, which would be white and granular, to settle, then stir in some paper pulp and filter. Wash the filter with cold water, incinerate the paper, ignite slowly to  $900^\circ \text{C}$  (to avoid reduction to Zn which is volatile, or volatilizing the  $\text{ZnO}$ ), and weigh as zinc oxide; yellow when hot, but white when cold, if pure. To find the per cent zinc, multiply the weight of the oxide by 80.339 and divide by 10, the weight of sample taken.

**Notes.** Following the separation of the zinc, several methods are available for its final determination. Thus, it may be dissolved in  $\text{HCl}$ , the solution made neutral to methyl orange with ammonia, heated, and the zinc precipitated with diammonium phosphate filtered, washed with water and 50 per cent alcohol, dried at  $135^\circ \text{C}$ , and weighed as  $\text{ZnNH}_4\text{PO}_4$  containing 36.64 per cent Zn; or the dry  $\text{ZnNH}_4\text{PO}_4$  may be gradually ignited to  $950^\circ \text{C}$  and weighed as  $\text{Zn}_2\text{P}_2\text{O}_7$  containing 42.90 per cent Zn.

The zinc sulphide may be converted to the sulphate and weighed as such.

If the percentage of zinc in the steel is appreciable (over 0.05 per cent), the volumetric method may be used. In this method, the zinc as  $\text{ZnCl}_2$  is obtained in a hydrochloric acid-ammonium chloride solu-

tion and titrated with a standard solution of potassium ferrocyanide. In this method, the ferrocyanide forms the insoluble  $K_2Zn_3(Fe(CN)_6)_2$  and either diphenyl-benzidine or orthophenanthroline ferrous complex is a satisfactory indicator.

### Procedure Separating Iron and Zinc with Ammonia

This method is well suited for the determination of zinc in ores, and in steel containing 0.005 to 0.06 per cent of zinc requiring a sample not exceeding 5 g. For zinc over 0.05 per cent, a sample of 1 or 2 g is recommended, when the acids used for the initial solution can be proportionately decreased. A blank must be carried through the whole series of operations.

### Separation of Iron

Treat 5 g of the sample in a 400-ml beaker with 15 ml  $H_2SO_4$  (1:1) and 90 ml of water. Cover, heat gently till the cuttings dissolve, and filter, if necessary, as for molybdenum steels and cast iron. Cool somewhat and add 50 ml of 20-per cent solution of ammonium persulphate. Boil 8 minutes and dissolve any manganese oxides formed by adding  $H_2SO_3$  drop by drop. Boil 2 minutes, dilute to 200 ml, and pour the warm solution with constant stirring into 95 ml of a solution containing 25 ml of water, 70 ml of ammonia, and 4 g of ammonium sulphate. Let the precipitate settle a few minutes, filter rapidly, and wash 1 to 4 times according to the percentage of zinc present with a mixture of 40 parts ammonia, 960 parts water, and 2 g of ammonium sulphate. Discard the precipitate and boil the filtrate down to 150 ml.

### Separation and Determination of Zinc

Add 2 drops of methyl orange indicator solution (0.1 per cent), neutralize with dilute  $H_2SO_4$  (1:1), add 7.5 ml excess, and pass  $H_2S$  for 1 hour. Let settle and filter through a close paper. Wash with 1-per cent  $H_2SO_4$  saturated with  $H_2S$ , boil to the expulsion of  $H_2S$ , and cool to 20° C, filtering again if a precipitate appears. Add methyl orange indicator solution, neutralize with dilute ammonia (1:1), and add 1 ml of *N*  $H_2SO_4$  for each 100 ml of solution to give a 0.01 *N* acid solution. Cool, pass  $H_2S$  for 1 hour, let stand 3 hours, and filter through a close paper containing a little paper pulp. Wash 10 times with cold water and ignite the paper and precipitate at a low temperature in a weighed porcelain crucible, burning the paper without flaming and gradually raising the temperature to 900° C. Cool, weigh as  $ZnO$ , and subtract the blank. Multiply the difference by 80.339 and divide by the weight of sample taken to find the per cent zinc.

### Procedure Separating Iron With Ether

Dissolve 25 g of the sample with 200 ml of diluted  $HCl$  (3 acid to 1 water) in an 800-ml Pyrex beaker, filter, if necessary, and oxidize the



ferrous iron by adding with constant stirring 30 ml of dilute  $\text{HNO}_3$  (1:1) and heating to boiling. Boil the solution down to about 50 ml, add 30 ml of  $\text{HCl}$ , and repeat the evaporation to 50 ml. Add 250 ml of dilute  $\text{HCl}$  (sp. gr. 1.11) and cool to room temperature. Transfer the solution to a separatory funnel, cool to  $5^\circ \text{C}$ , add 550 ml of anhydrous ethyl ether supplied in glass containers, shake the funnel 1 or 2 minutes, and let the 2 liquids separate for 10 minutes. Draw off the lower aqueous layer into the original beaker and evaporate off the excess ether on a water bath. Boil down to 50 ml, add 14 ml of dilute  $\text{H}_2\text{SO}_4$  (1:1) and 15 ml of  $\text{HNO}_3$ , boil 1 to 2 minutes, evaporate to fumes, and fume for 4 or 5 minutes.

### Separation of Iron With Ammonia

Cool the beaker and contents, add 100 ml of  $\text{H}_2\text{O}$ , heat gently, and pour the warm solution into 100 ml of dilute ammonia (1:1) containing 5 g of ammonium sulphate. Filter, wash, and treat the filtrate for the separation and determination of zinc as directed in the preceding method.

### General References

- Bright, H. A., Research Paper No. 664, *Natl. Bur. Standards J. Research*, 12, No. 3.  
Williams, C. E., and Sullivan, J. D., *Metals and Alloys*, 3, 240 (1932); 4, 151 (1933).  
Fairhall, L. T., and Richardson, J. R., *J. Am. Chem. Soc.*, 52, 938 (1930).

# Determination of Cerium

## Introductory Remarks

Cerium is one of the group of the rare-earth metals which has been added to steel. The element is now obtainable for use as an addition to steel in the form of ferrocerium, so that use of the element in certain steels at least may be emerging from the experimental stage. Methods for its determination, therefore, have not been thoroughly studied and standardized.

The first step in its determination generally involves a separation from all or most of the iron, and following such separations, the cerium will be found associated with the aluminum, titanium, zirconium, if a separation is made by either extraction or by some method depending upon hydrolysis.

Cerium, along with any other rare earths, may be separated from aluminum, titanium, zirconium, etc., by treatment with hydrofluoric acid which will leave the rare earths as an insoluble residue and dissolve the other elements. The rare-earth fluorides can next be converted to sulphates with concentrated sulphuric acid and precipitated with oxalic acid. The oxalates may then be ignited to the oxides and weighed. The procedure is briefly given as follows:

## Outline of Method for the Determination of Cerium

### Procedure

Referring to the methods given under the heading of *Chemical Separations*, dissolve 2 to 5 g of the sample in a proper acid and separate most of the iron with ether or with sodium bicarbonate, preferably the former. If the ether separation is used, drive the ether from the acid solution by heating gently, then add sulphuric acid and continue the heating to expel hydrochloric acid. Dilute the solution and adjust the acidity, if necessary, with ammonium hydroxide for the complete separation of iron, etc., by electrolysis over a mercury cathode. Conduct the electrolysis as described for the separation of vanadium. When all the iron has been separated along with chromium, nickel, copper, cobalt, molybdenum, etc., draw the solution from the salt in the usual manner. Heat almost to boiling and precipitate the cerium, aluminum, etc., in ammonium hydroxide. Boil the slightly ammoniacal solution 1 minute and filter through a paper supported in a rubber or Bakelite funnel. Dissolve the precipitate with hydrofluoric acid (48-per cent) and collect the solution in a platinum dish. Evaporate the

solution until it will solidify on cooling, then redissolve by digesting with 5 ml of HF and 50 ml of water. Filter the solution through a close paper supported in a Bakelite funnel and wash 2 or 3 times with hydrofluoric acid diluted with 10 volumes of water. Transfer the paper to a platinum dish, add 5 ml of concentrated sulphuric acid, and heat gently to destroy the paper and dissolve the rare-earth fluorides. Finally heat until the acid is fuming strongly, adding more acid if necessary, then cool and dilute to 50 ml, neutralize the solution with ammonium and add 1 to  $1\frac{1}{2}$  ml of  $\text{H}_2\text{SO}_4$  to make the solution about 0.5 *N*, and heat to boiling. Add 1 to 2 g of oxalic acid dissolved in a minimum volume of hot water. Let the solution stand 12 hours or longer, then filter through a close paper and wash the filter with hot water containing a little oxalic acid with 1 or 2 drops of sulphuric acid. Ignite the filter and precipitate slowly until the paper is burned, then at a higher temperature until the weight is constant, which procedure will give the cerium as the white oxide,  $\text{CeO}_2$ . Cool, and weigh the crucible. Multiply by 81.40 and divide by the weight of sample used to obtain the per cent cerium.

# Appendix I

## Determination of Sulphur or Carbon and Sulphur by Combustion in Oxygen

The accurate determination of sulphur in certain highly alloyed steels without the application of empirical factors or other corrections of an order comparatively large, when considered in relation to the sulphur present, has long been a problem which has been attacked along many different lines. We began to consider the problem in 1926, but could make no headway until a high-temperature furnace was made available. The first attempts to solve the problem by combustion in oxygen were made prior to 1925 in France and Germany, and for some years it appears the method was on an empirical basis, the gases being passed through a solution of  $\text{KIO}_3$  and the sulphur estimated from the iodine liberated. This method was investigated in 1930 by C. E. Nesbitt, who found it unreliable. Concurrently, Wirtz developed the method for carbon whereby all the gases from the combustion are collected, measured, passed through  $\text{KOH}$  solution, and the C estimated from the volume of  $\text{CO}_2$  absorbed. Combining this method with the method for sulphur by combustion, Holthaus and Seuthe pass the gases first through a mixture of  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$  which oxidizes the  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  to react with the  $\text{NaOH}$ , the excess of which in turn is titrated with a standard solution of  $\text{NaOH}$ . This method was investigated in 1937 by L. P. Chase, who found that, with the latest improved type of apparatus, satisfactory results can be obtained. The apparatus provides a high-temperature filter for the removal of fumes and an assembly consisting of an absorption chamber and burettes most convenient for visual titrations. In 1935, Kar<sup>1</sup> proposed leading the evolved gases directly into a solution of  $\text{Na}_2\text{O}_2$ , which is subsequently acidified with  $\text{HCl}$  and the sulphur precipitated with  $\text{BaCl}_2$  and weighed as  $\text{BaSO}_4$ . This procedure increases the time of a determination by introducing the more or less troublesome precipitation with  $\text{BaCl}_2$ .

Next, the method was investigated by Hale and Muehlberg,<sup>2</sup> who used the apparatus and method given in one of the procedures below. Since  $\text{SO}_2$  is absorbed by rubber and  $\text{SO}_3$  may pass through the absorbent if the gases bubble through it, these investigators aimed to avoid possible loss of  $\text{SO}_2$  and  $\text{SO}_3$ , by passing the gases directly into a dispersing device immersed in a neutral solution of  $\text{H}_2\text{O}_2$  contained in a special absorber, in which the  $\text{H}_2\text{SO}_4$  is titrated directly with a standard

solution of NaOH containing methyl red as indicator. With these refinements, the method gave results from 5 to 8 per cent low when applied to authoritative standard samples, the sulphur values of which had been determined by evolution and wet oxidation methods.

These studies, and others not formally reported, revealed the following defects in the method:

1. Any selenium or tellurium in the steel is oxidized to  $\text{SeO}_2$  and to  $\text{TeO}_2$ , both of which are evolved with the  $\text{SO}_2$ , the first subliming at  $250^\circ \text{C}$  and the second at about  $700^\circ \text{C}$ . Neither, however, markedly affect the sulphur result.

2. Besides these two oxides, oxides of As, Bi, Cd, Cs, Cu, In, Mo, Na, P, Pb, Sb, Tl are either volatilized or sublimed at the temperatures of this combustion, and may be carried along with the gas stream. Not all of these elements occur in steel, but others may be present in varying percentages.

3. The intense heat of combustion of the sample may volatilize other oxides that boil or sublime at temperatures above the tube temperature, or the rapid evolution of  $\text{CO}_2$  may cause "spitting" and projection of oxide as dust from the fusion, and these are caught up and carried forward by the gas stream. For example, positive evidence was at once obtained that some  $\text{Fe}_2\text{O}_3$  is carried into the absorption vessel.

If the oxygen is passed as rapidly as possible, the finely divided oxides (2) and (3) are wetted to a limited extent only, and most of the fume passes out of the absorber unless a high temperature filter is interposed. At slower speeds, more is retained, and since the oxides are all basic with respect to  $\text{H}_2\text{SO}_4$ , varying amounts of the acid may be fixed so that it is not titrated with the dilute NaOH solution, though some, like  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ , produced at high temperature, are not attacked by the dilute acid in the short time of contact. Slowing down the rate of flow of oxygen reduces the quantity of fume carried over, but gives low results evidently due to the formation of a greater proportion of  $\text{SO}_3$  which passes through the absorber as  $\text{SO}_3$  mist.

4. Apparently some  $\text{SO}_3$  is formed under any conditions when the sample is burned in pure oxygen, and this gas tends to condense on the walls of the tubing before it reaches the absorber, a trace being found even in the end of the combustion tube, which has a temperature gradient of about  $900^\circ \text{C}$  to  $150^\circ \text{C}$ . Traces may also pass through the absorbent as  $\text{SO}_3$  mist, and this tendency appears to be increased if the oxygen mixture contains moisture.

5. All steels contain a trace of nitrogen and some may contain up to 0.2 or 0.3 per cent. In a combustion, the nitrides in the steel are surely decomposed, but it is not certain whether the combustion results in the formation of  $\text{N}_2$  or of some of the oxides of nitrogen when the combustion takes place in pure oxygen. If certain of these oxides are formed, they may be retained by the absorbing solution

to be titrated with the NaOH solution, or they may catalyze  $\text{SO}_2$  to  $\text{SO}_3$ .

6. At the high temperature of combustion, the steel burns to  $\text{Fe}_2\text{O}_3 \cdot x\text{FeO}$ , forming a basic viscous slag, which reacts with most boat materials and traps some of the gases evolved. The latter defect is largely overcome by the addition of a little tin to the sample and spreading the latter in the boat.

7. With tin added, fusion of the sample takes place at lower temperatures and there is the temptation to let the temperature drop. In experiments with this method, we found that when the sample is placed in the boat in a pile and burned at  $1050^\circ \text{C}$  almost one-third of the sulphur remained with the fusion as sulphate. Much less was found at  $1150^\circ \text{C}$ , but a temperature higher than  $1200^\circ \text{C}$  was necessary to reduce the sulphur held by the fusion to a point that gave no precipitate with  $\text{BaCl}_2$  in slightly acid solution reduced with stannous chloride, pure zinc, or pure aluminum. No tests were made to determine if the sulphur was all evolved at a lower temperature when tin is used as an accelerator.

With these various sources of error recognized, the method was made a subject for exhaustive study during 1937 by T. S. Woodward and Dr. H. J. Wolthorn, who investigated its possibilities not only as applied to the determination of sulphur in steel but also to the determination of this element in other materials, such as ores and slags containing no fluorine. In their work, these investigators found that all sulphates can be decomposed by heat alone in an atmosphere of nitrogen to give all the sulphur as  $\text{SO}_2$ . They also abandoned the use of indicators for titrating the evolved acidic gases, and resorted to direct potentiometric titration of the  $\text{SO}_3$  formed from the  $\text{SO}_2$ , which is absorbed in a dilute solution of  $\text{H}_2\text{O}_2$ . By the use of a glass electrode and a fixed end point of pH 5, they avoid errors due to  $\text{CO}_2$  absorption by the solution. Then by controlling the rate of gas flow, also the speed of combustion through the proportion of oxygen in the nitrogen-oxygen gas mixture used to sweep the  $\text{SO}_2$  out of the tube, always using a minimum percentage of oxygen, they reduce to a negligible amount the fume, or finely divided solids and sublimates carried over into the absorbent solution. Through these factors, combined with the very steep temperature gradient obtained through the type of tube and furnace employed, they also completely avoid catalytic oxidation of  $\text{SO}_2$  and reduce the  $\text{SO}_3$  formed to an indeterminable amount. In this work, the possibility of determining carbon and sulphur on the same sample was ignored, and attention was centered on the control of conditions necessary for the accurate determination of sulphur.

From this discussion, it is evident that this method for sulphur, like the combustion method for carbon, permits various modifications in apparatus and procedure, but that certain requirements must be rig-

idly met to obtain the desired accuracy in the results. For this reason, the three methods developed by members of this committee are given in chronological order and in detail to permit others to check the procedures and duplicate the results obtained by them.

### Procedure of Hale and Muehlberg

#### Apparatus and Reagents

A sketch of the apparatus is shown in Fig. 18, from which it will be seen to resemble very closely the assembly for the determination of carbon alone. However, certain parts are of special design and others must be made of certain materials only, the search for which explains the time required to perfect the apparatus and procedure. Therefore, the whole assembly is described piece by piece and in detail, following the plan for the carbon apparatus. Arrangements have been made whereby the apparatus may be obtained complete, or essential parts may be ordered separately.

##### A. Oxygen Supply

##### B. Reducing Valves

**C. Oxygen Purifying Train.**—All parts are precisely the same as the corresponding parts previously described for carbon.

**D. Pressure Regulator and Auxiliary Oxygen Supply.**—This apparatus replaces the mercury gauge used by some chemists on the carbon train. It consists of a rubber bag in a container which limits its expansion and functions to provide a reservoir of oxygen for the complete combustion of the sample and maintain the pressure constant to prevent "suck back" of the oxidizing solution in J when the sample burns. It is so constructed that during the preignition period it becomes filled with oxygen at a pressure slightly greater than that required to force gas through the train; and, during the ignition, it supplies this oxygen to the tube at the same pressure and as rapidly as the sample consumes it. This simple device makes it unnecessary to adjust the flow during ignition, and will operate the same irrespective of the varying back-pressure from the absorption apparatus. Without it manual manipulation of the valves during a combustion is necessary.

**E. Electric Furnace.**—This furnace is similar to the high-temperature furnace recommended for carbon, but for this purpose the furnace must be capable of giving operating temperatures as high as 1350° C, as temperatures above 1200° C are required to drive off the sulphur quickly from the fusion. With many alloy steels, lower temperatures give low results for sulphur, and low results are the rule for all steels burned at lower temperatures unless tin is used as an accelerator and other special precautions are taken.

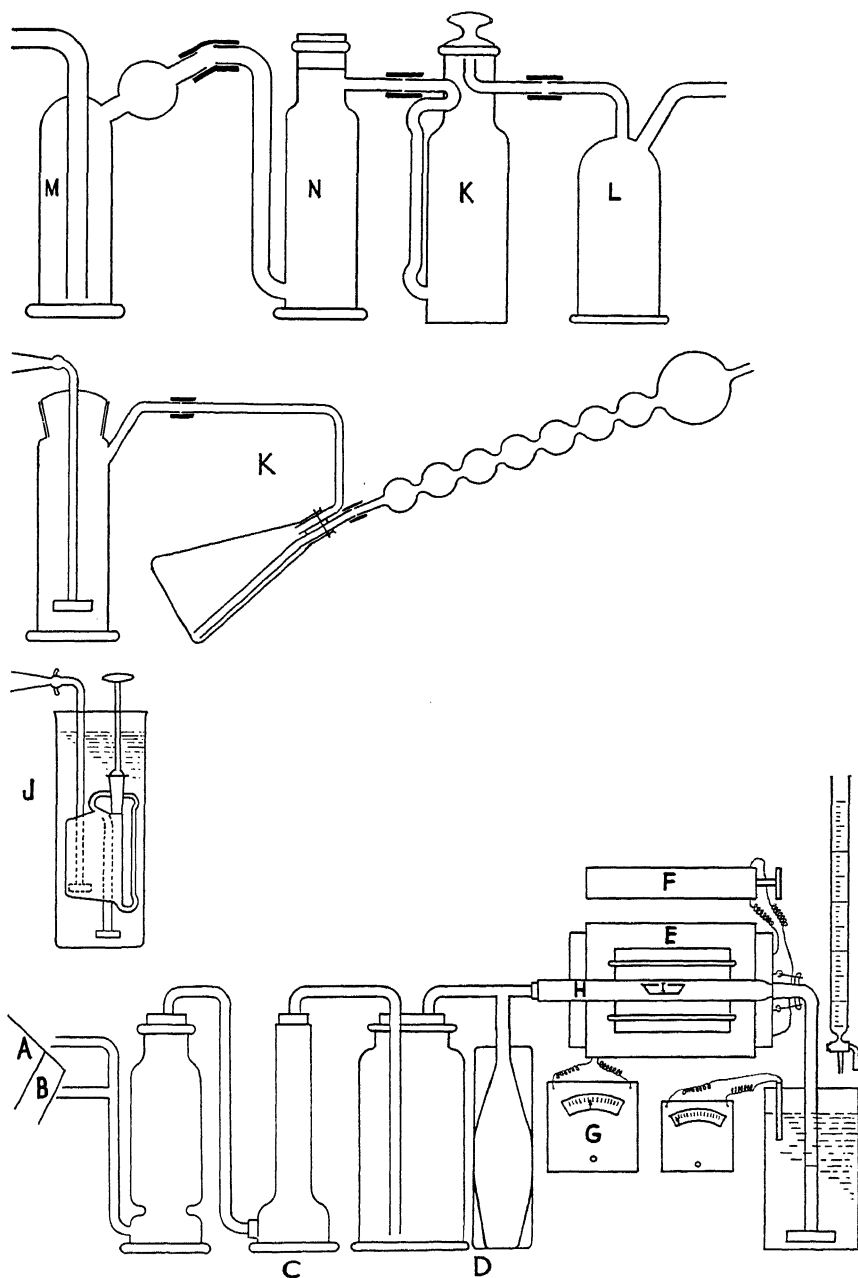


FIGURE 18. Diagram of apparatus for the determination of sulphur or of sulphur and carbon by combustion in oxygen by the Hale-Muehlberg method. (See also figure 9.)



**F.-G. Rheostat and Pyrometer.**—These items of equipment serve the same purpose as in the determination of carbon and may be of any type suitable for the work.

**H. Combustion Tube.**—Only an unglazed vitrified tube of porcelain may be used. Any other type is either affected by the high temperature or tends to react with the  $\text{SO}_2$  evolved. As to size, a tube 1 inch or  $1\frac{1}{8}$  inches in diameter inside and 27 or 28 inches long has been found most satisfactory. If suitable provision is made at the intake end to admit the oxygen or oxygen-nitrogen mixture without the use of a rubber stopper, the length may be reduced to 25 inches. To prevent condensation of  $\text{SO}_2$  or  $\text{SO}_3$ , the exit end of the tube is kept hot by locating it near the furnace. A tube with a double reduced end, as shown in Fig. 19 below, appears best, since it permits the shortest coupling with the lowest temperature at the end. If a 1-inch tube is used, the double step-down in diameter may not be necessary. Since rubber of all kinds absorbs sulphur dioxide rapidly, it cannot be used to connect the tube to the sulphur absorber J. Also, to avoid chance of condensation of  $\text{SO}_2$  or  $\text{SO}_3$ , the exit end of the tube is kept somewhat hotter than is usual in determining carbon alone. To overcome these difficulties, connection between the combustion tube and the sulphur absorber is made by means of a ground joint, as shown in Fig. 19. By carefully standardizing the taper and every detail of the grinding of both the porcelain and the glass tube, the parts have been made interchangeable, so that a gas-tight joint is obtained between any tube connected to any standard absorber. The joint is seated and held firmly in place by means of spiral springs, 4-4, anchored to the safety shield of the furnace and extending to lugs, 3-3, on the inlet tube of the absorber. Hooks on the ends of the springs make it easy to slip them over the lugs, 3-3, with two quick motions of the hand.

**I. Combustion Boat.**—With the exception of the combustion tube itself, the boat is the next most important part of the equipment and must be made of special materials. The workers were unable to find a sulphur-free bedding that would not produce a slag that would hold the oxides of sulphur in large bubbles or gas pockets, making it impossible to drive off all the sulphur without prolonging the heating for indefinite periods after combustion has taken place. With no bedding, the boat must be made of material that will not soften at steel melting temperatures, will not alloy with iron or combine with oxides of iron, chromium, nickel, silicon, and will not react with oxides of sulphur or selenium. The nickel boat commonly used will not meet these requirements, nor will most of the refractory boats commonly used; and it was found necessary to develop a special boat, which is made by the McDanel Refractories Company. This boat is rectangular in shape,  $3\frac{7}{8}$  inches long,  $\frac{3}{4}$  inch wide, and  $\frac{3}{8}$  inch deep, outside dimensions, with flat bottom and thin walls at right angles to it to give maximum flat-

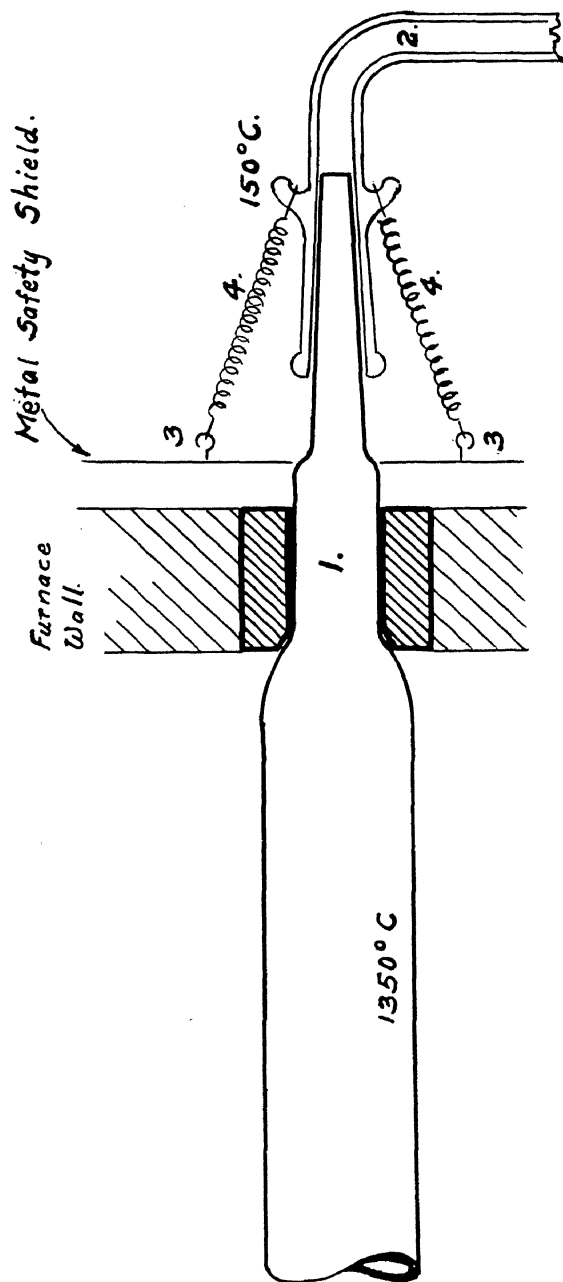


FIGURE 19. Drawing of special combustion tube designed for use in the determination of sulphur or sulphur and carbon by combustion. The exit end (1) of the tube is ground to fit within the glass tube (2), which is held in place by coiled springs 4-4 attached to lugs 3-3. This tube and the furnace walls are designed to give the greatest possible temperature drop between the hot zone and the tip of the tube without water-cooling

bottom area inside. Woodward and Wolthorn found that pure  $\text{Cr}_2\text{O}_3$  can be used as a bedding to permit 2 to 4 determinations to be made in the refractory boat and the use of a boat made of heat-resistant low-sulphur 28-per cent chromium steel.

**J. Sulphur Absorber.**—The principles of this apparatus were developed by experiments at the Research Laboratory. Its form and construction are shown in Fig. 18. The tube ground to fit over the end of the combustion tube, as described under H above, conducts the gases to a bubbler constructed of fritted glass and located near the bottom of the vessel. Here the gases bubble through a 0.5-per cent neutral solution of hydrogen peroxide, which oxidizes the  $\text{SO}_2$  to  $\text{SO}_3$  and retains the acid in solution. Since the top of the vessel is closed by a ground glass stopper sealed to the inlet tube, the excess oxygen bearing only the  $\text{CO}_2$  escapes through the side tube, from which it passes to the  $\text{CO}_2$  absorber, if it is desired to determine the carbon also. The object of the fritted glass filter is to divide the stream of gas into an infinite number of small streams, and may be replaced with a finely perforated disc of platinum. Experiments have shown that only a part of the sulphur is held by the solution if the gas is passed through the solution in large bubbles. Since the solution is rendered distinctly acid by the  $\text{SO}_2$  gathered, it retains none of the  $\text{CO}_2$ , even that which would normally dissolve in the water being swept out by the  $\text{CO}_2$ -free oxygen passed after the combustion of the sample is complete.

**K.  $\text{CO}_2$  Absorber.**—Since J removes all the sulphur and does not retain any of the  $\text{CO}_2$ , the carbon may be determined either volumetrically or gravimetrically by the use of appropriate apparatus. In Fig. 18, the apparatus for determining the carbon volumetrically is shown attached to the sulphur absorber. That shown is known as the Brady-Kiefer type, in which a 1.0 to 1.2-per cent solution of barium hydroxide is used to absorb the  $\text{CO}_2$ , the excess barium hydroxide being titrated with a standard acid.

When it is desired to determine the carbon gravimetrically, the water vapor carried by the gas must be completely removed, and the simple absorber K is replaced by the train MNKL, in which M and N contain the desiccants. The object of M is to remove the greater portion of the water, leaving only a portion to be removed by N, which of necessity must be packed with the same desiccant as is used in K. A combination suggested is concentrated sulphuric acid in M and anhydrous, dehydrate or phosphorus pentoxide in N.

**L. Flow Indicator.**—The flow indicator is needed only as a protection to the  $\text{CO}_2$  absorber. For the gravimetric method it contains sulphuric acid; for the volumetric method, barium hydroxide solution.

## Reagents for Absorption and Titration of Sulphur

### Hydrogen Peroxide Solution (0.5-per cent)

Hydrogen peroxide (30-per cent) .....	17 ml
Water to make .....	1000 ml

This solution is prepared every 12 hours or oftener from the best grade of 30-per cent hydrogen peroxide available. Fifty ml of this solution are used for each determination and are neutralized just before use with the standard sodium hydroxide solution.

The acid and alkali solutions used for titrating the sulphur are preferably standardized so that 1 ml will be equivalent to 0.01 per cent sulphur. Hence, the exact concentration will depend upon the weight of sample used, which in turn depends upon whether or not it is desired to determine the carbon gravimetrically. If only sulphur is to be determined, or if carbon is also to be determined by the volumetric method, the weight of sample recommended for carbons under 0.50 per cent and sulphur under 0.300 per cent is 1.6 g. With this weight of sample, the solutions are made 0.01 *N* and 1 ml equals 0.01 per cent sulphur. With higher carbon or higher sulphur, a 0.8-g sample is recommended, when the 0.01 *N* solution is equivalent to 0.02 per cent sulphur.

When carbon is determined gravimetrically along with the sulphur, 1.6 g of sample may be used, and the weight of CO<sub>2</sub> multiplied by 17 to find the per cent carbon, or 1.3636 g of sample may be used and the sulphur titrating solutions adjusted to a normality of 0.008525 so that 1 ml will be equivalent to 0.01 per cent S.

**Standard Sulphuric Acid** (0.01 *N* 1 ml = 0.01 per cent S on 1.6 g sample)

Sulphuric Acid (sp. gr. 1.84) .....	0.3 ml
Water .....	1000.0 ml

The water is boiled to expel CO<sub>2</sub> and cooled to a standard temperature (20° C for winter, 25° C for summer), and the acid is added with a 5-ml or 10-ml pipette calibrated to read to 0.05 ml. This solution will be slightly too concentrated.

An alternative method is to dilute 100 ml of a 0.1 *N* solution to 1 liter, but this solution may prove either too dilute or too concentrated.

The solution may be standardized against purified sodium carbonate as described in "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Coal, Coke, and By-Products," or against acid potassium phthalate through the sodium hydroxide solution, but it is preferable to standardize the acid direct by precipitating the sulphur from a measured portion with BaCl<sub>2</sub> and weighing the BaSO<sub>4</sub> when the

$$\text{Normality} = \frac{\text{weight of BaSO}_4 \times 1000}{116.71 \times \text{ml of solution used}}, \text{ or the}$$

$$\text{Weight of sulphur per ml} = \frac{\text{weight of BaSO}_4 \times .1374}{\text{ml of solution used}}$$

To standardize, 100 ml of the acid and 100 ml of water are each transferred separately to 200-ml beakers. Exactly 10 ml of the acid and 2 ml of hydrochloric acid are added to each, the solutions are heated to boiling, and 10 ml of a 10-per cent solution of barium chloride are added. After digesting until the precipitates have settled, they are filtered off upon close papers and washed free of chloride with hot water, then ignited and weighed. The weight of the blank subtracted from the weight of the BaSO<sub>4</sub> from the 110 ml of acid gives the weight of BaSO<sub>4</sub> equivalent to 100 ml of the solution.

**Standard Sulphuric Acid** (0.08525 *N* 1 ml = 0.01 per cent S on 1.3636 g sample)

Sulphuric Acid (sp. gr. 1.84) .....	0.26 ml
Water (CO <sub>2</sub> -free) .....	1000.0 ml

An alternative method is to dilute 85.25 ml of an 0.1 *N* solution to 1 liter.

The solution is standardized as described above for the 0.01 *N* solution. It is understood that the acid solution is kept at the standard temperature prior to, and following, its standardization.

### Methyl Red Indicator Solution

#### Formula 1

Ortho-carboxybenzene-azo-dimethylaniline .....	0.025 g
Water (hot, CO <sub>2</sub> -free) .....	100.0 ml

The water is heated to boiling and cooled slightly before the reagent is added. The solution is allowed to stand till cool, and filtered rapidly. From 5 to 6 drops per 50 ml of titrating solution are used for titrations. A satisfactory solution is also prepared as follows:

#### Formula 2

Methyl Red .....	0.1 g
Ethyl Alcohol (85- to 95-per cent) .....	60 ml
Water (CO <sub>2</sub> -free) .....	40 ml

The reagent is dissolved in the alcohol, which is preferably redistilled from a mixture of quicklime and sodium hydroxide, and diluted with the water. Since the transition point is affected slightly by the alcohol, it is recommended that exactly 3 drops be used for all titrations for sulphur by this method.

The indicator gives a red color at pH 4.2, an orange color at pH 5, and a yellow color at pH 6.3. Between pH 5 and 6, the color varies from orange to a greenish yellow, according to the kind or source of light. Hence, the necessity of selecting a definite end point, which

for this work is preferably the orange-red. Since the transition points are slightly affected by the  $\text{CO}_3$  ion, water free of  $\text{CO}_2$  or carbonates is used. Other factors affecting the transition points are the concentration of the indicator in, and the temperature of, the titrating solution.

**Standard Sodium Hydroxide** (0.01 *N* 1 ml = 0.01 per cent S on 1.6 g sample)

Sodium Hydroxide .....	0.41 g
Water ( $\text{CO}_2$ -free) .....	1000.0 ml

The water is boiled and cooled, and the NaOH is dissolved in about 25 ml, then diluted to 1000 ml with  $\text{CO}_2$ -free water at the standard temperature. The NaOH should be reasonably free of carbonate, but the usual addition of an excess of  $\text{Ba}(\text{OH})_2$ , followed by filtration, to remove it is not advisable. If the NaOH contains more than a trace of carbonate, a few drops of a saturated solution of  $\text{Ba}(\text{OH})_2$  are added, the solution is allowed to stand 6 to 10 hours, then filtered rapidly, and sufficient neutral  $\text{Na}_2\text{SO}_4$  solution to precipitate the barium is added. After the  $\text{BaSO}_4$  has settled out, the solution is filtered, and diluted to 1 liter with  $\text{CO}_2$ -free water at the standard working temperature. This solution should be kept protected from the air with a  $\text{CO}_2$  trap. Dilute solutions of NaOH react with many kinds of glass, hence are liable to change. Bottles coated with a neutral wax have been tried, but frequent titrations against the standard acid are desirable.

To standardize the solution, 10 ml of the standard sulphuric acid are added to 50 ml of  $\text{CO}_2$ -free water, the required number of drops of the methyl red indicator solution are added, and the solution is titrated with the NaOH solution to the disappearance of the red color, which is always taken as the end point. On the alkaline side, the color is a light greenish yellow, difficult to see. At the selected end point, the red color should return on the addition of one drop of the acid.

#### Solutions for Determining Carbon Volumetrically

For the determination of carbon volumetrically, the following solutions must be provided:

**$\text{CO}_2$ -free Water.**—A large supply must always be at hand.  $\text{CO}_2$  may be removed from distilled water by passing purified air through it, or by boiling for several minutes. After driving off the  $\text{CO}_2$ , the water is kept in a vessel closed with a 1-hole stopper bearing a tube packed with soda lime or ascarite to prevent it from absorbing  $\text{CO}_2$  or other acidic gases from the air.

#### Barium Hydroxide Solution

Barium Hydroxide ( $\text{Ba}(\text{OH})_2$ ) .....	11 g
Water, free of $\text{CO}_2$ .....	1000 ml

This solution is prepared by dissolving the  $\text{Ba}(\text{OH})_2$  in 250 ml of boiling water, cooling, filtering rapidly, and diluting to 1 liter with  $\text{CO}_2$ -free water. The solution is kept protected with a  $\text{CO}_2$  trap. Each determination requires 50 ml.

#### Standard Hydrochloric Acid Solution

Hydrochloric Acid, concentrated .....	6 ml
Water, free of $\text{CO}_2$ , to make .....	1000 ml

Like the barium hydroxide solution, the acid should be kept protected with a  $\text{CO}_2$  trap. Both solutions are usually made up in large quantities to avoid frequent standardization, and this practice requires that they be fully protected and used at a standard working temperature.

#### Indicator Solution

Phenolphthalein .....	0.2 g
Ethyl alcohol (50-per cent, 100 proof) .....	100.0 ml

This solution must be neutral to the indicator. If it is colorless, add  $\text{NaOH}$  solution until it is a slight pink color. The alcohol is best redistilled from quicklime and sodium hydroxide and diluted with  $\text{CO}_2$ -free water. More concentrated or less concentrated solutions and a greater or smaller number of drops may be used, but as the end point is affected by the concentration of the reagent and the alcohol in the titrating solution, it is extremely important that exactly the same amount be used in each determination and in standardizing the solutions.

The solutions are compared and the carbon value of the acid solution is found as follows:

To find the acid equivalent of the barium hydroxide solution exactly 50 ml of the latter are transferred to a 500-ml flask, diluted with 100 ml of  $\text{CO}_2$ -free water, and titrated, after the addition of 3 drops of phenolphthalein indicator, to a colorless end point with the acid solution. The titration is repeated twice, and the average of three closely agreeing results is recorded as the blank. This titration is repeated at intervals of 2 to 5 days, according to conditions, to make sure this relation has not changed.

The carbon value of the acid is found by the use of standard steels, which are run through all the steps of a regular determination. For this purpose, a series of standards is best used, including one containing 0.10 per cent carbon or less; one from 0.20 to 0.30 per cent carbon; another 0.40 to 0.50 per cent; a fourth with 0.70 to 0.85 per cent; and a fifth 1.00 per cent carbon or more. The standard values used are those determined with standards containing about the same carbon as the steels to be analyzed.

After combustion of the sample and absorption of the  $\text{CO}_2$  evolved, the excess barium hydroxide is titrated with the acid, as described

under the heading *Procedure*. The number of ml of the acid solution so used is subtracted from the number obtained in titrating the blank, and the difference is divided into the per cent carbon in the standard to find the carbon value of ml of the acid equivalent to the barium hydroxide neutralized by the  $\text{CO}_2$  evolved. Three or more portions of the same standard should be thus run through, and the average of three closely agreeing results used as the carbon value of the acid.

**Testing and Care of the Combustion Train.**—After the apparatus has been assembled for the determination of sulphur alone, or for both sulphur and carbon, the latter either volumetrically or gravimetrically, it should be thoroughly tested, with the following objects in mind:

1. To make sure it is gas-tight throughout at operating temperatures and pressures. This can be done by sealing the exit end, admitting oxygen slowly to the operating pressure, then closing off the oxygen and observing the pressure drop.

2. To make sure that the apparatus and oxygen used will give no blank. To test for blanks, blank runs, with only the sample of steel omitted, are made until the cause of the blank, if any, has been found and corrected. With a new setup, carbon blanks are likely to be more troublesome than sulphur blanks.

3. To determine if the train and conditions are right to give all the sulphur and all the carbon. This point is best determined by analyzing standard samples of steel of approximately the same composition as the steels to be analyzed regularly. The conditions most important are temperature, time and speed of aspirating after combustion has taken place, and material of which the boat is constructed. If the temperature is not high enough, rapid combustion of the sample will not be complete, and both sulphur and carbon results will be low. Low results, for sulphur in particular, may be expected if the aspirating is continued for too short a time or at too slow a rate. On the other hand, the sulphur result may be too low and that for carbon too high, if the oxygen is forced through the train too rapidly after burning the sample. If the boat is not made of proper material, the oxides will flux it, and the semi-fused mass will hold back some of the sulphur. The same retention of sulphur by the fusion occurs if too large a sample is used, or if the drillings are placed in the boat in a heap or in heaps. Best results are obtained with the drillings scattered over the bottom of the boat in a single layer.

Fairly accurate results have been obtained by using tin as an accelerator, and operating at slightly lower temperatures. In addition to causing the sample to ignite and burn more rapidly, tin also affects the fusion following combustion, causing the fusion to form a solid mass free of gas bubbles.

Some iron oxide fume is carried over into the absorber, especially if the oxygen flow is rapid during combustions, but this does not mate-



rially affect the results, if not excessive. These fumes tend to clog the frit glass bubbler, which, however, is easily cleaned with dilute hydrochloric acid.

**Correct Temperatures for Different Steels.**—As to the exact temperatures to use, these may vary according to the kind of steel being analyzed and the time available for aspirating, and since it is desirable to operate at as low temperatures as possible to prolong the life of heating elements, it is useful to know the lowest temperatures that can be used successively with different steels. Assuming that no tin or other accelerator is used, the lowest operating temperatures for a number of steels and other operating data are given as follows:

Kind of Steel	Wt. of Sample	Lowest Temperature	Rate of O <sub>2</sub> Flow	Total Time of Passing O <sub>2</sub>
Plain-Carbon Steels	1.6 g	1205° C (2200° F)	250 ml per min.	12 minutes
Low-Alloy Steels	1.6 g	1260° C (2300° F)	250 ml per min.	12 minutes
18-8	1.6 g	1344° C (2450° F)	250 ml per min.	12 minutes
24-per cent Chromium	1.6 g	1400° C (2552° F)	250 ml per min.	12 minutes
High-Speed	1.6 g	1371° C (2500° F)	250 ml per min.	12 minutes

Steels of the last type, with or without nickel, and some other very high-alloy steels will not give up all the carbon they contain unless an accelerator, such as tin shot, is added to the portion of sample used for the combustion. With 0.2 to 0.5 g of tin added, all the carbon is given off at a somewhat lower temperature than 1200° C, 1150° C being the minimum permissible. Hence, the addition of tin and a temperature of 1200° C to 1250° C is recommended for steels containing more than 20 per cent chromium or more than 30 per cent total alloying elements.

At these temperatures combustion of the steel is complete within 3 minutes after pushing the boat into the hot zone and turning on the oxygen. The rest of the time is required to sweep the SO<sub>2</sub> and CO<sub>2</sub> into the absorbing apparatus, which will depend upon the maximum flow that can be maintained. The maximum flow in turn will depend upon the porosity and the condition of the bubbler in the sulphur absorber and the method used for determining the carbon. In the gravimetric method for carbon, the maximum flow through the bubbler governs, while in the volumetric method, the maximum flow the CO<sub>2</sub> absorption bulbs will permit is the controlling factor.

**Procedure.**—With the apparatus and solutions in readiness and the temperature of the combustion furnace adjusted to the kind of steel to be analyzed, the several steps of a determination are varied for each of three possible cases as follows:

*Case I.*—*Sulphur alone to be determined.* First make sure that the sulphur absorber is perfectly clean and otherwise in good condition. If the bubbler appears to contain much oxide fume, add a little warm dilute HCl (1:2) through the intake tube, then rinse thoroughly with

distilled water until the washings are neutral to the methyl red indicator.

Then transfer 50 ml of the hydrogen peroxide solution to the absorber and add the required number of drops (6 or 3 of the alcoholic solution) of the methyl red indicator. If the solution is red in color, as it generally is, due to a trace of acid in the peroxide, add standard sodium hydroxide solution drop by drop until one drop just dispels the red color, which is taken as the end point. If this point is over-titrated, add one or more drops of the standard sulphuric acid, and adjust the end point with the standard sodium hydroxide solution.

Next, transfer 1.6 g (0.8 g if sulphur is over 0.3 per cent) to a clean combustion boat, spreading the drillings or chips over the bottom so that they lie in as nearly a single layer as possible. If tin is required as an accelerator, spread 0.15 to 0.2 g of the shot (20-mesh) over the sample, distributing it as evenly as possible.

Push the boat into the combustion tube for a distance of 2 or 3 inches, and attach the sulphur absorber to the exit end of the tube, making sure that all parts are held firmly together with the rubber bands and the coiled springs provided for the purpose. Finally, push the boat into the hottest zone of the tube, insert the stopper, and turn on the oxygen to flow at the rate of about 300 ml per minute. Continue to admit the oxygen at this rate for 10 minutes. The solution in the sulphur absorber will suddenly turn red in color as soon as the evolved  $\text{SO}_2$  reaches it.

It requires approximately 490 ml of oxygen to burn 1.60 g of steel; consequently, this supply is insufficient when combustion begins, but that accumulated in the reservoir previous to combustion supplies the deficiency. The volume of a combustion tube 1" I. D.  $\times$  27" long is about 335 ml, so that with oxygen fed at 300 ml per minute to displace all the gases in the tube following complete combustion of the sample with oxygen flowing at 300 ml per minute requires about 1.1 minutes, if there is no backward diffusion. Since 2 to 3 minutes are required to preheat and completely burn the sample and as the gas in the tube should be replaced at least twice, the minimum time for a combustion is about 5.5 minutes. If the flow of oxygen is slower or the tube is larger, the time must be increased accordingly. For example, if the flow is decreased to 200 ml per minute in this example, the displacement time is increased almost to 1.7 minutes.

In addition to these factors, 2 or 3 minutes additional are apparently required to "boil" all the sulphur out of the slag formed, and if the chips are placed in one pile in the boat, this time is considerably increased, possibly to as much as 30 minutes if the temperature is on the low side.

When sufficient time has elapsed to sweep all the sulphur out of the tube, turn off the oxygen and disconnect the absorber. Then pull

the boat out of the furnace and discard it. In removing the boat, do not let it rest in the cold end of tube as it may crack the tube, but pull it out at one stroke and without a stop upon the receiving tray held just under and in front of the opening.

To titrate the sulphuric acid formed in the absorber, add the standard 0.01 *N* sodium hydroxide solution slowly until the color changes, raising and lowering the intake tube and bubbler to stir the liquid. When the red color fades, raise the bubbler out of the solution to permit the liquid in the tube to drain out, which will change the color of the solution to red again. Now add more of the sodium hydroxide solution until the end point is reached, raise the bubbler out of the solution and rinse it thoroughly by introducing CO<sub>2</sub>-free water into the tube, which rinsing will cause the solution to turn red again.

At this point, add the sodium hydroxide drop by drop, stirring between drops by raising the bubbler out of the solution, until one drop dispels the red color. If the solution is exactly 0.01 *N* and 1.6 g of sample were used, the number of ml used gives the sulphur in hundredths of a per cent. Otherwise, multiply the number of ml used by the sulphur titer of the solution, multiplied by 100, and divide by the weight of sample used.

The titrated solution is poured from the absorber and replaced with another 50 ml of the hydrogen peroxide solution preparatory to another determination. No rinsing of the absorber is necessary except after cleaning with acid.

*Case II—Sulphur and Carbon to be determined, both volumetrically.* Prepare the sulphur absorber as directed in Case I above, and transfer the sample to a thoroughly ignited boat. If the carbon expected is under 0.60 per cent, use 1.6 g of sample; if more than 0.60 per cent, use 0.8 g of sample.

*Procedure.* Transfer exactly 50 ml of the standard barium hydroxide solution to the Erlenmeyer flask of the CO<sub>2</sub> absorption apparatus, making sure that both the flask and the bulbs are clean and absolutely free of either acid or alkaline substances.

Push the boat into the tube of the furnace for a distance of 2 or 3 inches, attach the sulphur absorber to the exit end of the tube, and connect the CO<sub>2</sub> absorption apparatus to the outlet of the sulphur absorber. Using a clean steel rod, push the boat into the hot zone of the tube, close the opening, and admit the oxygen gradually until it is passing through the CO<sub>2</sub> absorber as individual bubbles following each other as rapidly as possible. Since the rate of flow is between 200 and 250 ml per minute, continue to pass the oxygen for 15 minutes to make sure all the SO<sub>2</sub> and CO<sub>2</sub> has been swept out of the combustion tube and absorbed in their respective absorption vessels.

At the end of aspirating period, turn off the oxygen, wait until gas ceases to bubble through the CO<sub>2</sub> absorber, then disconnect it and

the sulphur absorber in turn before opening the tube and withdrawing the boat.

Titrate the sulphur as directed under Case I above.

Raise the  $\text{CO}_2$  absorber to a vertical position, and when all the solution has drained into the Erlenmeyer flask, loosen the stopper and rinse the bulbs thoroughly with  $\text{CO}_2$ -free water, using from 40 to 50 ml for this purpose. To the flask, add 3 drops of phenolphthalein solution and titrate carefully to the disappearance of the red color, being careful not to over-titrate. Deduct the number of ml of the acid used from the number equivalent to the 50 ml of barium hydroxide solution and multiply this difference by the proper per cent carbon value of 1 ml to find the per cent carbon in the sample.

*Case III—Sulphur and Carbon to be determined, the latter gravimetrically.* In this case, either 1.6 g or 1.3636 g of sample may be used for all steels containing less than 0.3 per cent sulphur, irrespective of the percentage of carbon present. If the sulphur titrating solutions are adjusted to give the per cent sulphur direct with this weight of sample, use of the factor weight for carbon is recommended.

After making sure that the temperature of the furnace is raised to the point required by the kind of steel to be analyzed, weigh the sample carefully and transfer it to a thoroughly ignited boat. If the steel is one of the very high-alloy heat-resistant types requiring an accelerator, spread 0.1 to 0.2 g of 20-mesh tin shot over the bottom of the boat with the sample. Insert the boat, push it forward 2 or 3 inches, and leave it in the open end of the combustion tube to warm it somewhat.

Weigh the  $\text{CO}_2$  absorption bottle, full of oxygen under a pressure adjusted to that of the balance case, and connect it to the drying train.

Transfer 50 ml of the hydrogen peroxide solution to the sulphur absorber, add the methyl red indicator solution, neutralize, and connect the absorber to the combustion tube, as described under Case I.

Connect the sulphur absorber to the first drying tube of the  $\text{CO}_2$  train, push the boat containing the sample forward into the white-heat zone, close the combustion tube, and admit the oxygen as rapidly as it can be bubbled through the sulphur absorber without forming continuous streams of gas through the solution. Continue to pass the gas at a uniform rate for 10 to 15 minutes.

The exact time cannot be stated, because the time necessary depends upon the size of the combustion tube used, the rate of flow of the oxygen, the porosity uniformity of the glass frit in the sulphur absorber, and the amount of unfilled space left in the drying train between the sulphur absorber and the  $\text{CO}_2$  absorber. With this unfilled space reduced to a minimum, frit glass of uniform porosity, and a combustion tube giving a minimum volume to be displaced, a gas flow of 250 to 300 ml per minute should be possible and the maximum time

required should not exceed 10 minutes. Therefore, the minimum time must be experimentally ascertained for each set-up.

At the end of the period prescribed for continuing the flow of the oxygen, close the valves; and when the gas flow through the sulphur absorber slows down, disconnect it from the  $\text{CO}_2$  train, also disconnect the  $\text{CO}_2$  absorber and place it in the balance case. Then disconnect the sulphur absorber from the combustion tube, remove the stopper, and withdraw the boat with a single stroke.

Titrate the  $\text{H}_2\text{SO}_4$  in the absorber as directed under Case I and record the result in terms of per cent sulphur, calculating it from the sulphur titer of the standard sodium hydroxide solution, if necessary.

Now open the  $\text{CO}_2$  bottle momentarily, if it is of the closed type, and weigh it against its counterpoise. If the carbon factor weight was used, the difference in weights multiplied by 20 gives the per cent carbon. If 1.6 g of the sample were used, the difference in weights multiplied by 17 gives the per cent carbon.

#### **Procedure of Woodward and Wolthorn for the Determination of Sulphur in Carbon and Low-Alloy Steels and Nonmetallic Substances**

##### **Application and Principles of the Method**

This method is designed for the determination of sulphur in carbon and low-alloy steels and certain nonmetallic substances, whether the latter are combustible or noncombustible. With reference to the latter, it affords a quick, convenient method for the determination of sulphur in substances which are very difficult to analyze for sulphur by ordinary methods. Whatever the nature of the substance, all the sulphur is evolved as  $\text{SO}_2$  into a solution of hydrogen peroxide and determined by direct titration with a standard solution (usually 0.01 *N*) of  $\text{NaOH}$ , the titration being made preferably by potentiometric methods. For potentiometric titrations, the use of  $\text{H}_2\text{O}_2$  to oxidize the  $\text{SO}_2$  to  $\text{SO}_3$  is necessary, because the  $\text{SO}_2$ , apparently, is not capable of combining with water to give an equivalent number of hydrogen ions. By adapting the conditions to the nature of the material being analyzed, the authors have succeeded in causing the equipment to function without a plus or minus blank error. Furthermore, in analyzing pure substances, such as  $\text{Na}_2\text{SO}_4$ , they have obtained results that agree with the theoretical values, and are able to duplicate results on other substances that lend themselves to thermal decomposition in a neutral or an oxidizing atmosphere and do not yield, besides  $\text{SO}_2$ , other volatile acidic products, such as fluorine or chlorine, that interfere with the direct titration of  $\text{H}_2\text{SO}_4$ . In certain respects, therefore, the method is varied for different substances or classes of substances as follows:

**For all materials** the decomposition is effected at a temperature of  $1300^{\circ}\text{C}$  or higher in order to assure complete dissociation of  $\text{SO}_3$ . Although larger quantities may be determined, for highest accuracy an effort is made to hold the sulphur per determination below 1 mg, and the maximum rate of evolution to less than 0.1 mg per minute.

**For metallic materials**, such as carbon and low-alloy steels, the authors make use of air, or of oxygen and nitrogen mixed in various proportions, instead of oxygen alone, to control the speed of combustion. By keeping the rate of combustion of the sample sufficiently slow to avoid a boat temperature but slightly above that of its surroundings, spattering is avoided and little or no metallic oxide fume is produced to be deposited in the tubing between the combustion boat and the absorber. To insure a low concentration of  $\text{SO}_2$  in the gas stream, the flow of gases through the tube during and immediately following the combustion is maintained at a rapid rate (approximately 1 liter per minute). The low concentration of  $\text{SO}_2$  and of  $\text{O}_2$  in the gases, the absence of catalyzing solids in the exit end of the tube, the rapid passage of the gases through the short catalyzing temperature zone, and the quick cooling through the temperature range from  $1000^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  contribute to prevent the formation of  $\text{SO}_3$  and assure a maximum recovery of the  $\text{SO}_2$  in absorption, provided the gas stream is finely dispersed through the absorbing solution.

With reference particularly to steels, samples of plain-carbon steels may be burned in air if the weight of the sample is reduced from 1.6 g to 1 g for steels containing more than 0.060 per cent sulphur. Larger samples of high-sulphur steels may be used if the oxygen in the  $\text{O}_2\text{-N}_2$  mixture is reduced to about 15 per cent by volume, and a longer time is allowed for evolving the sulphur. High-speed steels are analyzed by combustion in air. For alloy steels that are difficult to burn in air, such as low chromium-nickel (2- to 3-per cent) steels, the temperature of combustion is raised to  $1350^{\circ}\text{C}$ , an oxygen-nitrogen mixture containing 40 to 50 per cent  $\text{O}_2$  is used and a longer time is allowed for the combustion. With this larger proportion of oxygen care must be exercised that the combustion does not take place too rapidly, a condition usually making itself manifest by rapid evolution of  $\text{SO}_2$  and the appearance of  $\text{SO}_3$  mist escaping the absorber. When this mist appears, results seldom fail to be 10 to 20 per cent low. Efforts to control the combustion rate of heat resistant and stainless steels through the proportion of oxygen used in the mixture were not completely successful.

Mixtures of oxygen and nitrogen required are conveniently prepared by exhausting the oxygen in a tank to a given pressure, connecting to a tank of nitrogen under high pressure, and admitting nitrogen to the oxygen till the pressure of the latter reaches that as predetermined from the proportions desired.

**For Nonmetallic Substances.**—The method is successfully applied to oxidized mineral substances, such as slags, or any other substances containing alkali or alkaline-earth compounds of sulphur, provided they contain no fluorides, which evolve fluorine or other interfering elements or oxides by igniting the sample in an atmosphere of nitrogen at a temperature of  $1300^{\circ}\text{C}$ , the weight of sample being regulated in accordance with the sulphur content as indicated above. Combustible substances are ignited in air or an  $\text{O}_2\text{-N}_2$  mixture containing less oxygen than air. In general, the method is applicable to all compounds of sulphur, provided the amount of sample taken for analysis can be regulated to evolve the  $\text{SO}_2$  at a rate not in excess of the maximum as stated above.

### Method of Standardizing the NaOH

A distinctive feature of the method is the fact that the NaOH solution used for the titrations is standardized by a direct method, involving the ignition of a pure sulphate,  $\text{Na}_2\text{SO}_4$ , and titration of the evolved  $\text{SO}_2$ . To make sure that all parts of the equipment are functioning without error, the normality of the NaOH solution thus obtained may be checked against a standard sulphuric acid solution (0.1 *N*) and is made the basis for calculating the sulphur content of the samples analyzed.

### Procedure in Titrating

Another distinctive feature is the method of titrating. All titrations are conducted in the absorbing beaker and without disconnecting the absorber from the combustion tube. In fact titrations are carried out starting as soon as combustion of the sample starts without interrupting the operation, the bubbling gas serving to stir the solution. After titrating the  $\text{SO}_2$  evolved over a fixed period, the operation is continued for another, shorter period to test its completeness; and the solution is then titrated to the final end point, after sucking liquid up the tube to the joint to rinse it. Thus, many titrations extending over a day or more may be made in the same absorbent and without disconnecting the absorber or otherwise disturbing the arrangement of the parts.

### Absorption Equipment

For absorbing the  $\text{SO}_2$ , the simple apparatus described in the preceding method may be used if the  $\text{SO}_2$  concentration is kept low. The essential part consists merely of a tube with a small chamber at the base covered with fritted glass to break up the gas stream into a great number of smaller streams and bubbles. This part is immersed in the absorbing solution of  $\text{H}_2\text{O}_2$  contained in a tall form beaker in which the titrations are made. The upper end of the tube is formed and ground inside to fit over the ground end of the combustion tube as





shown in Fig. 19, page 315, thus forming a gas-tight ground joint which permits the end of the combustion tube to be kept at a temperature of 150° C to 200° C to prevent condensation of SO<sub>2</sub> or SO<sub>3</sub> within the end of the combustion tube.

Fig. 20 shows a special type of double absorber used during the development of the method. With fine frit glass this absorber gives a back-pressure about twice that of a single absorber, but this defect can be remedied by using larger openings, and the apparatus may be found useful for work giving higher concentrations of SO<sub>2</sub> than are encountered in analyses of steels. If determinations are conducted in strict accordance with instructions regarding rate of flow of gas and the concentration of oxygen to control the rate of combustion, a single absorber immersed in H<sub>2</sub>O<sub>2</sub> solution contained in a beaker suffices.

### List of Equipment

The combustion apparatus is similar to that described for the preceding method. (See Fig. 18.) With some changes in the arrangements of parts, as will be described later, a list of the parts required is as follows:

- 1 globar tube furnace, inside length of heating chamber 9 to 13 inches.
- 1 platinum-platinum-rhodium thermocouple with suitable indicator to serve as pyrometric equipment.
- 1 McDanel combustion tube with small end ground to an interchangeable joint.
- 1 glass delivery tube with ground joint to fit combustion tube at one end, and at the other, a fritted Jena glass disc to serve as a means for breaking up the gas stream.
- 1 300-ml Pyrex beaker, tall form, for containing the absorbing solution.
- Boats and bedding material, McDanel unglazed combustion boats; number as required.
- 25-per cent chromium steel boats, low sulphur. These boats are optional, the life of each being limited to a small number of determinations. Formed of 18- or 20-gauge sheets.
- Cr<sub>2</sub>O<sub>3</sub>, technical grade, powdered, ignited until a representative sample gives no blank for sulphur.
- 1 purifying train, including an alkaline absorber and a drying agent.
- 1 mercury manometer.
- Suitable implements of Nichrome or similar material for manipulating the boats, consisting of a wire with hook on one end, and a pan for receiving the hot boats.
- 1 precision burette for titrating, 50 ml capacity.

- 1 or more volumetric flasks, 1000 ml capacity, exactly calibrated.
- 1 ripper weighing burette.
- 1 Muencke water blast air pump, or other means for supplying clean air at a pressure up to 40 inches of water or more.

*Optional Equipment*, depending upon method of titration selected and materials to be analyzed.

- 1 pH electrometer with glass electrode and extension cable.
- 1 tank or bottle of compressed nitrogen.
- A flexible tube, fitted with suitably threaded attachments for transferring compressed gases between high pressure cylinders.

These items are assembled and arranged to form a conveniently workable train as follows:

1. A source of air or nitrogen at a pressure of about one pound.
2. Connections which are made of glass tubing, using as little rubber as possible.

3. Purification apparatus. Calcium chloride and soda lime towers of generous size are sufficient, unless there is contamination with oil. In the latter case, the air is heated to the ignition temperature and cooled before purification. A side connection is made to the line near the point where it enters the furnace. This connection is closed with a pinchcock and the side tube is extended to a point near the delivery end of the furnace. By means of this connection and suitable manipulation of pinchcocks, the flow of gas may be interrupted and the furnace pressure varied for washing.

4. The combustion tube is of such a length as to allow the entering end to remain below 50° C and its location is such as to maintain the delivery end at 200° C or higher.

5. A furnace with heating chamber 9 to 13 inches long is found suitable.

6. The absorber. The tapered ground joint is held satisfactorily by a spring attachment and the special fritted glass absorber enters a 300-ml Pyrex beaker of tall form containing the absorbent solution to a depth of three to four inches above the frit. The same portion of the solution may be used for a number of determinations. The absorber solution is a 0.5- to 1.0-per cent solution of  $\text{H}_2\text{O}_2$  containing a few drops of the indicator if titrations are to be made visually. If a pH meter is available, the glass electrodes are inserted in the solution and the indicator is omitted. With the indicator, the pH of the solution is adjusted to the preferred end point; with a pH meter, all solutions are titrated to an end point of exactly pH 5.

The  $\text{Cr}_2\text{O}_3$  bedding material is ignited thoroughly in a muffle, preferably for several hours, and the boats and bedding are ignited at the regular furnace temperature before they are used. With the  $\text{Cr}_2\text{O}_3$  bedding, one porcelain boat will usually serve for 2 or 3 determina-

tions before it breaks, while one of the chromium steel boats can ordinarily be used for about 10 determinations before a blank shows the steel has begun to give up its sulphur in amounts that can be detected.

With the apparatus assembled and connected, it is tested for leaks at all joints and for blank as follows: The furnace is gradually heated to the required temperature of 1300° C. A boat and bedding are inserted into the tube, and the air or gas mixture is admitted at the rate of 1 liter per minute. The blank is considered satisfactory, when not more than 0.05 ml of 0.01 *N* NaOH solution is required to restore the solution to its original pH value after the gas has passed for a period of 20 minutes.

### Solutions Required

**Sulphuric Acid, 0.1 *N*.**—Dilute 2.8 ml concentrated  $\text{H}_2\text{SO}_4$  to 1 liter and determine its normality to 1 part in 1000 by the  $\text{BaSO}_4$  method, using 50 ml for the determination.

**Standard Sulphuric Acid Solution, 0.01 *N*  $\text{H}_2\text{SO}_4$ .**—Deliver into a flask, accurately graduated to contain 1 liter, from an exact burette, a number of ml of the 0.1 *N*  $\text{H}_2\text{SO}_4$  equal to 10 divided by the exact normality and dilute to the mark.

**Standard Sodium Hydroxide Solution, 0.01 *N* NaOH.**—In a Pyrex glass bottle or flask, dissolve 0.42 g best grade NaOH in water and dilute to 1 liter. Balance this solution against the 0.01 *N*  $\text{H}_2\text{SO}_4$  and adjust the volume if necessary, repeating the operations until the two solutions are within 0.1 per cent of each other. In making these titrations, stir the solution with a brisk current of purified air and select an end point within the range of pH 5 to 5.5. Rebalance these solutions each week and readjust the NaOH solution if and when it is found out of balance.

**Hydrogen Peroxide, 0.5 to 1.0 per cent.**

**Standard Sodium Sulphate Solution.**—0.1 *N*  $\text{Na}_2\text{SO}_4$  standardized for weight burette.

Recrystallize  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , dry it by applying heat gently, and finally ignite it at 800° C. Cool and transfer approximately 0.72 g of this material accurately weighed to a tared dry liter flask. Fill the flask with water and weigh the solution accurately. From this weight calculate the weight of sulphur per gram of solution.

**Methyl Red.**—Dissolve 0.1 g in 60 ml ethyl alcohol and dilute with water to 100 ml.

### Procedure

**Testing the Equipment and Technique with Standard Sodium Sulphate Solution.**—Using a weight burette, transfer to one of the ignited porcelain boats approximately 0.5 g of the standard  $\text{Na}_2\text{SO}_4$  solution, evaporate the solution to dryness in a drying oven, and dry it at 100° C for 15 to 20 minutes. From the weight of this solution evaporated,

calculate the weight of sulphur it contains. With the furnace at a temperature of  $1300^{\circ}\text{C}$ , insert the boat into the tube, and pass the purified nitrogen or air through the tube at the rate of one liter per minute for ten minutes. Turn off the flow of gas through the tube and release the pressure by opening the side tube, thus allowing the absorber solution to flow back through the fritted glass base of the delivery tube. With the gas flowing through the apparatus at the usual rate, titrate the solution in the absorber to the adopted end point. Stop the gas flow, again rinse the tube by releasing the pressure, and titrate the solution to the end point. Permit the gas to flow a few seconds, rinse the delivery tube thoroughly by drawing the solution up to within an inch or so of the ground joint by carefully applying suction to the side tube. Admit the gas again and make the final fine adjustment of the end point. To make sure the decomposition of the sodium sulphate is complete, continue the gas flow for 5 minutes longer and repeat the rinsing of the tube and titration adjustment. To find the sulphur recovered, multiply the ml of standard  $0.01\text{ N NaOH}$  solution used by  $0.00016\text{ g}$ .

### Variations in the Procedure for Sulphur in Steels

For the determination of sulphur in steels, the equipment is manipulated and the titrations are made in the same way as described for sodium sulphate above. Directions covering other details that need attention are briefly given as follows:

**The Sample.**—For best results, use clean fine cuttings, preferably those remaining upon a No. 60 and passing through a No. 20 sieve.

**Weight of Sample.**—For plain and low-alloy steels containing less than 0.060 per cent sulphur, use a factor weight of  $1.6\text{ g}$  of sample.

The number of ml of the standard  $0.01\text{ N NaOH}$  used to titrate the evolved oxide of sulphur, divided by 100, then gives the per cent sulphur in the sample.

For steels containing a higher percentage of sulphur, use only the finest cuttings and reduce the weight of sample to  $1\text{ g}$ , or to  $0.8\text{ g}$ , if the sulphur is above 0.150 per cent. To find the per cent sulphur, multiply the ml of  $\text{NaOH}$  solution used by  $0.00016\text{ g}$  and this product by 100 times the weight of sample used.

If no bedding is used in the boat, spread the sample over the bottom of a porcelain boat.

If the  $\text{Cr}_2\text{O}_3$  bedding is used, spread it to a depth of at least  $\frac{1}{8}$  inch in the boat, which may be either one of the special porcelain boats or one made of 25- to 28-per cent chromium steel, and spread the sample evenly upon the bedding. Burn the sample at a high temperature— $1300^{\circ}$  or over—and with as low a percentage of oxygen in the  $\text{O}_2\text{-N}_2$  mixture as will give complete combustion, that is, 15 to 20 per cent for plain steels and 21 to 25 per cent for low-alloy and high-speed steels. For steels that fail to burn under these conditions, raise the

temperature to 1350° C and increase the percentage of oxygen up to 50 per cent if necessary.

In very exacting work, burn two or more portions of the sample upon a bedding of  $\text{Cr}_2\text{O}_3$  contained in a porcelain boat, carefully remove the burned cuttings after each combustion, grind them in a mortar, and reburn the combined portions to make sure they retain no residue of sulphur.

**Procedure as Used by L. P. Chase, South Works,  
Carnegie-Illinois Steel Corporation**

**Apparatus.**—This method requires special apparatus differing somewhat from that described in the preceding sections. The method and apparatus are briefly described as follows: The sample is burned in a high-temperature tube furnace with oxygen; the products of combustion are conducted through a filter to remove the fume; the  $\text{SO}_2$  formed in the combustion is absorbed in a solution of hydrogen peroxide containing a measured quantity of a standard solution of sodium hydroxide; and the excess  $\text{NaOH}$  is titrated with a standard solution of sulphuric acid of the same normality as the  $\text{NaOH}$ , the difference thus being taken as equivalent to the sulphur in the sample of steel. The high-temperature furnace is of the usual type capable of giving temperatures of 1300° C, but the tube is of small diameter—one inch or under. The exit end of this tube is connected through a short piece of rubber tubing about 8 inches long to another tube of larger diameter which is heated with a second furnace to a temperature between 280° F and 300° F, which is determined and regulated by a high temperature mercury thermometer. The larger tube contains the filter, which is of the bag type made of heat resistant fibers. After passing through the filter the gases are conducted through rubber tubing to the absorption vessel which is made part of an assembly of apparatus referred to by the distributors as the “determinator.” Other parts of the determinator consist of a 30-ml overflow pipette, a 5-ml overflow pipette, and a 5-ml overflow titrating burette, all arranged to discharge into the absorption vessel. The absorber is of the simple bubble type, the gas being admitted through 4 or 5 small openings at the end of the delivery tube which enters the titrating vessel near the bottom so that the gas will bubble upward through the absorbent solution. Thus the same vessel serves as an absorber and a titrating beaker. All parts rest in a fixed position, so the absorber is equipped with a drain tube, and all stirring is accomplished by bubbling gas through the solution, a rubber bulb being connected through a 3-way stopcock for this purpose. This apparatus and the low-temperature furnace and filter are distributed by the Laboratory Equipment Corporation, St. Joseph, Michigan.

The acid burette for titrating the excess sodium hydroxide solution has a capacity of 5 ml as noted above. Its small capacity and its

length permit it to be graduated to eightieths of a ml, each ml being divided into 8 main divisions and each main division into 10 smaller divisions. Therefore, each main division represents 0.010 per cent sulphur on one g of sample when the titration is made with 0.05 *N* solution. At South Works 0.025 *N* solutions are used, and the readings are divided by two.

With this apparatus, plain-carbon low-sulphur steels (under 0.050 per cent sulphur) can be burned at 1150° C, but it has been found that higher-sulphur carbon steels and practically all alloy steels require a temperature of 1250° C or over. In addition the use of tin as an accelerator is recommended.

The oxygen is passed through the tubing at a comparatively rapid rate, approximately 550 ml per minute through the absorption and titrating vessel, and during the combustion of the sample it is necessary to feed additional oxygen so that an excess is present to burn the sample quickly. Failure to feed the oxygen in this way is apt to give low results.

The auxiliary furnace, the function of which is to heat the tube containing the filter for the removal of oxides of iron, tin, etc., must be maintained at a temperature between 280° F and 300° F (approximately 150° C).

The oxygen supplied should be dry, and it may be desirable under some conditions to pass it through a drying tower packed with "Anhydron," or a similar drying agent.

### Special Solutions Required

**Hydrogen Peroxide (0.05 per cent).**—Dilute 20 ml of 30-per cent  $\text{H}_2\text{O}_2$  to 1 liter.

**Standard Sodium Hydroxide, Methyl Red Solution—(0.025 *N*).** Dissolve 1.01 g of pure NaOH in water. Also, dissolve 0.02 g of methyl red indicator in 500 to 600 ml of water contained in a 1-liter volumetric flask. Add the NaOH solution and dilute to 1 liter.

Titrate 20-ml portions of this solution with the standard sulphuric acid and adjust the volume to a normality of 0.025.

**Standard Sulphuric Acid (0.025 *N*).**—Dilute 1.3 g (0.71 ml) of concentrated acid (sp. gr. 1.84, Baumé at 60° F 66.15°) to 1 liter. This proportion is approximately correct for 66-degree acid. If the acid has a specific gravity of exactly 1.84, this solution will be slightly too concentrated.

To standardize the solution, heat 50-ml and 100-ml portions to boiling, add a drop or two of HCl to each, and precipitate the sulphate ion by adding 2 to 4 ml of a 10-per cent solution of barium chloride dropwise while stirring constantly. Permit the beakers to stand at a temperature near boiling until the precipitate has settled, filter through a close paper, and wash with hot water until the paper is free of chlorides. Ignite slowly to a temperature of 950° C and weigh as

$\text{BaSO}_4$ . The weight of  $\text{BaSO}_4$  multiplied by 0.42017 gives the equivalent weight of  $\text{H}_2\text{SO}_4$ . For a 0.025 *N* solution this product should equal 0.001225 times the number of ml used for the titration.

### Procedure

With these solutions and equipment, assuming that the apparatus has been assembled and it and the solutions tested, directions for making determinations as applied to steels containing less than 0.1 per cent sulphur are briefly given as follows:

To determine the exact quantity of the 0.025 *N* NaOH solution equivalent to 5 ml of the 0.025 *N*  $\text{H}_2\text{SO}_4$ , make a blank test by adding to the absorption vessel 5 ml of the 0.025 *N* NaOH solution and 30 ml of the  $\text{H}_2\text{O}_2$  solution, passing oxygen through the train as in a regular determination, and titrating with the 0.025  $\text{H}_2\text{SO}_4$  solution to a red end point. Repeat the test till the exact volume of 0.025 *N* NaOH solution equivalent to 5 ml of the 0.025 *N*  $\text{H}_2\text{SO}_4$  has been determined and empty the absorption vessel.

Transfer 1 g of the sample to a high-temperature porcelain boat. Push the boat into the hottest zone (1250° C or over) of the combustion tube, insert the stopper, and permit the boat and contents to heat for the 20 to 30 seconds required to make up the absorbing solution. Add the standard NaOH solution (approximately 5 ml as determined above) equivalent to 5 ml of the 0.025 *N*  $\text{H}_2\text{SO}_4$  and 30 ml of the  $\text{H}_2\text{O}_2$  solution. Turn on the oxygen and maintain the flow, by hand during combustion of the sample, at approximately 550 ml per minute, through the exit of the absorber. After combustion of the sample is complete, continue the flow for 5 minutes at the same rate. Turn off the oxygen and titrate the excess NaOH with the standard 0.025 *N*  $\text{H}_2\text{SO}_4$  solution to the adopted red end point, using air forced through the solution by hand with the rubber bulb to stir the solution. Since the burette is graduated to read from zero upward, take the reading as equivalent to the NaOH neutralized by the  $\text{SO}_2$  evolved and divide by two to find the per cent sulphur in the sample.

### Text References

1. Kar, H. A., *Ind. Eng. Chem. (Anal. Ed.)*, 7, 244 (1935).
2. Hale, C. H., Jr., and Muehlberg, W. F., *Ind. Eng. Chem. (Anal. Ed.)*, 8, 317 (1936).

## Appendix II

### Discussion of Methods for Oxygen, or Oxygen, Hydrogen and Nitrogen in Steel

No methods for oxygen or hydrogen in finished steel are recommended in this volume for reasons apparent in the following discussions.

#### Vacuum Fusion Methods

In these methods the  $O_2$  in the steel is converted to CO by melting in a graphite crucible at  $1600^\circ C$  heated electrically by induction. The steel container is evacuated during the fusion and the gases analyzed either volumetrically or gravimetrically. There are various modifications, developed in Germany by Diergarten, Eilender, and Oberhoffer, and in this country by Jordan, Vacher, and Eckman of the Bureau of Standards, by Yenson and Ziegler of Westinghouse Research Laboratory, and more recently by Lewis Reeve, who reduced the time of a determination, after the apparatus has been set up and made ready, to 30 minutes for oxygen present as FeO and MnO, or about 5 hours for  $O_2$ ,  $N_2$ , and  $H_2$ .

The method has not yet been accepted as giving accurate results for all steels, particularly those containing much aluminum or titanium, though Reeve claims that by the use of tin to reduce the melting point of the steel sample and a temperature of  $1600^\circ C$ , total oxygen can be determined even in samples killed with aluminum.

Reeve's paper (Improvements in the Vacuum Fusion Method for the Determination of Gases in Metals, by Lewis Reeve, A.I.M.E. Contribution 56, Detroit Meeting, October, 1933) is abstracted briefly as follows:

I. The sample, in the form of a cylinder and mixed with about one-half its weight of tin, is enclosed in a graphite crucible and heated electrically by induction, the gases are drawn off by vacuum pump and analyzed in an Orsat apparatus. Time for a determination—5 hours.

II. Results of experiments on pure oxides, pure silicates, and on oxidized samples of iron deoxidized with Fe-Mn, Fe-Si, and Al, indicate FeO is reduced at  $1050^\circ C$ , MnO at  $1050^\circ C$  to  $1150^\circ C$ ,  $SiO_2$  at  $1300^\circ C$ , and  $Al_2O_3$  at  $1550^\circ$  to  $1600^\circ C$ .

III.  $O_2$  yields from pure oxides vary and are seldom 100 per cent. This inaccuracy is ascribed to loss from spattering and reaction of CO with metallic vapors, particularly aluminum.



IV. Even gray iron (C 3.2 per cent, Si 1.7 per cent, Mn 0.40 per cent) contained 0.047 per cent  $O_2$  as FeO and MnO.

V. The scheme of analysis involves calculating all the  $O_2$  given off as CO up to  $1050^\circ C$  to FeO; all the CO off from  $1050^\circ$  to  $1150^\circ C$  as MnO; all the CO off at  $1300^\circ C$  as  $SiO_2$ ; and all that given off between  $1550^\circ$  and  $1600^\circ C$  as  $Al_2O_3$ . This procedure gives results that check the electrolytic extraction method for  $SiO_2$ , but is slightly low for  $Al_2O_3$ .

VI. The accuracy of the method is taken to be about 0.002 per cent for  $O_2$  and  $N_2$ , and 0.0002 per cent for  $H_2$ .

VII. Nitrogen is evolved at all temperatures from  $1050^\circ$  to  $1570^\circ C$ , corresponding to iron and manganese nitrides, silicon nitride ( $Si_3N_4$ ), and aluminum nitride.

VIII. Evidence is presented to show that steel contains a small proportion (0.0006 to 0.001 per cent) of hydrogen, but not combined as a metallic hydride, while all of the  $O_2$  and  $N_2$  is present as oxides and nitrides.

The tendency of certain constituents of steels to volatilize at high temperatures, and to recombine with the evolved gases at lower temperatures, and before they reach the measuring part of the apparatus, appears as a source of error that will be extremely difficult to overcome. Finally, the problem of obtaining samples actually representative of a given lot of steel, and of preparing these samples in a manner to exclude any possible source of error, is one that baffles the most expert technicians.

### Hydrogen Reduction Method

This method is generally credited to Ledebur, and is commonly known as the Ledebur Method. In it the sample is heated to  $1100^\circ C$  to  $1200^\circ C$  in an atmosphere of hydrogen, and the water formed by the reaction of the  $H_2$  with FeO and MnO is collected and weighed, from which the per cent  $O_2$  in the steel is calculated. Several modifications of the method have appeared, the most important of which consists in the addition of tin to the sample. The tin lowers the fusion point below  $1200^\circ C$  and hastens the reaction between the hydrogen and the oxides in the steel. The latest modification is that of Larsen and Brower.<sup>1</sup> Suffice it to say, the method is not adapted to quick routine determinations, largely on account of the time required. In Germany, where the method has been most used, the quickest time made for a determination with apparatus of the simplest type and not approved as wholly satisfactory, using tin with the sample, is one hour and 40 minutes. The fact that a variable amount of the oxygen present as  $SiO_2$  may be evolved, and is so evolved at higher temperatures, along with that combined as FeO and MnO, introduces an element of uncertainty in the determination of the FeO and MnO in the finished steel.

### Methods Based on Determination of Oxides or Oxide Inclusions Held in the Steel in the Solid State

These methods are based upon the assumption that all the oxygen in the solid steel is combined and in the form of solid oxides, silicates, etc. The problem has been to find a way of dissolving or volatilizing the metallics of the steel, without in any way dissolving or changing the nature of the compounds of oxygen, which would then remain as a residue. Various methods to accomplish this end have appeared and are listed below.

#### The Iodine Method

This method is often referred to as the Eggertz Method, since it was first published by V. Eggertz in 1868. Since then various modifications have appeared, the latest being those of T. R. Cunningham and J. R. Price,<sup>2</sup> and J. J. Egan, W. Crafts, and A. B. Kinzel.<sup>3</sup> In the latter's modification, 5 g of sample are dissolved in an ice cold solution of ferrous iodide and ammonium citrate. The residue is filtered off, washed 20 times with cold and 5 times with hot 2-per cent ammonium citrate solution, and ignited at 1000° C. It is then analyzed for  $\text{SiO}_2$ ,  $\text{MnO}$ ,  $\text{FeO}$ , and  $\text{Al}_2\text{O}_3$  by usual methods.

Since the time required is more than 5 hours, the method is not suitable as a rapid control method. Besides, sulphides are decomposed leaving all the S in the residue, and elements such as Ti, Cr, V, and W interfere, as their carbides are also found in the residue. Carbides of Fe and Mn are decomposed. Phosphides are decomposed, and part of the phosphorus may be oxidized to  $\text{P}_2\text{O}_3$ , which is precipitated and gathered in the residue. Correction for P can be made by determining phosphorus in the residue.

#### The Chlorine Method

This method depends upon the fact that the chlorides of iron, silicon and manganese are volatile, and that dry chlorine gas reacts with the metallic iron, silicon, manganese, carbides, sulphides, phosphides, and nitrides in steel or iron heated to a proper temperature to form volatile compounds leaving a residue of oxides, silicates, carbon, and non-volatile chlorides. The method originated with Oersted, Berzelius, and Fresenius in 1825-27, and has since been studied by many investigators. Results may be summarized as follows: Ferric chloride and silicon chloride are volatile at 300° C. Manganese chloride and the chlorides of other alloys are volatile at higher temperatures ranging from 350° C to 800° C. At these higher temperatures the oxides are either acted upon by the chlorine or become unstable. Only  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  can be determined with accuracy by this method. Extreme care and several hours time are required for a determination.

### Electrolytic Solution Method

In this method the sample in the form of a small bar is made the anode of an electrolytic cell and partly dissolved by means of an electric current, a solution of ferrous sulphate being used as the electrolyte. Since 1930 this method has received much attention by C. H. Herty, Jr., and associates, Benedicks, and some members of this committee. As iron salts hydrolyze during the electrolysis the method does not serve for FeO, but only for SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Benedicks found objections to the use of ferrous sulphate as an electrolyte, and we found that Cr and Cu, if present, are left with the residue in some specimens of steel. These drawbacks and the time consumed in making a determination eliminate this method as a satisfactory one for control work.

### Mercuric Chloride Solution Method

In this method a solution of mercuric chloride is used to dissolve the metallic portion of the sample, leaving the oxides insoluble. While the method has been used and is recommended for metallic iron in ores, slags, etc., it has not attracted much attention as a method for inclusions in steel, and has shortcomings that put it in a class with the last three methods mentioned above.

## Acid Solution Methods

### The Nitric Acid or Dickenson Method

In the acid solution methods, the steel is dissolved in a dilute mineral acid, leaving a residue composed of SiO<sub>2</sub> or silicates and Al<sub>2</sub>O<sub>3</sub>, if no interfering alloying elements are present. The four acids, HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>, have been used with about equally satisfactory results. Dickenson (see Journal Iron and Steel Institute, 1926) used a 10-per cent cold solution of HNO<sub>3</sub> to dissolve the sample of very fine millings or drillings. Carbonaceous matter in the residue was oxidized with KMnO<sub>4</sub> solution, and basic salts of iron along with silicic acid were washed out with a 10-per cent solution of NaOH. C. H. Herty, Jr., and collaborators found that the method gives satisfactory results for SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, but it is very slow.

### The Sulphuric Acid Method

In discussing Dickenson's method, T. P. Colelough reported that he obtained higher recoveries with a 10-per cent solution of H<sub>2</sub>SO<sub>4</sub> than with HNO<sub>3</sub>. The time may or may not be shortened depending on the kind of steel to be treated.

### The Hydrochloric and Perchloric Acid Methods

The use of HCl, concentration about 5 *N*, was first described by F. O. Kichline (see Industrial and Engineering Chemistry, 1915).

Other investigators using the method are Oberhoffer and Ammann (Stahl und Eisen, p. 1536, 1927), L. Jordan, J. S. Acken, and H. A. Bright (Bureau of Standards). Finally, in 1930, it was made the basis of a new method for FeO in liquid steel by C. H. Herty, Jr., and associates. In 1933, W. D. Brown found that 70-per cent perchloric acid could be substituted for hydrochloric acid, and that the use of perchloric acid shortened the time of solution to a few minutes.

Applied to finished steel, none of the acid solution methods give all the oxygen present, especially when applied to rimming steel and semi-killed steels. Both FeO and MnO are completely decomposed and dissolved. About 70 per cent of the oxygen present as iron and manganese silicates is obtained in the residue. In steels completely killed with aluminum, more than 95 per cent of the  $O_2$  is obtained as  $Al_2O_3$ . The recovery is somewhat less in steels partly killed.

### Microscopic Method

This method consists in cutting small sections from the piece of steel under examination, polishing the surface to a high degree, and then examining the polished surface under a microscope. Under these conditions non-metallic inclusions of all kinds are clearly visible. But while the microscope has been very useful in the study of the grain or crystalline structure of steel and of the size, form, and nature of inclusions, it has insurmountable drawbacks as a means of quantitatively determining the inclusions. However, by carefully counting, observing the nature of, and measuring the size of the inclusions, estimations apparently near the truth have been made. The method at best is a tedious one, and cannot be considered as an instrument of control.

In a world-wide comparative study recently completed, the results obtained may be taken as verifying the statements above, which were written before these data were available.<sup>4</sup>

### Text References

1. Larsen, B. M., and Brower, T. E., "Critical Studies of a Modified Ledebur Method for the Determination of Oxygen in Steel," *A.I.M.E.*, Feb. 16, 1932.
2. Cunningham, T. R., and Price, J. R., *Ind. Eng. Chem. (Anal. Ed.)*, 5, No. 1 (1933).
3. Egan, J. J., Crafts, W., and Kinzel, A. B., *A.I.M.E. Technical Publication No. 498*, February, 1933.
4. Complete information on this work is given in Thompson, J. G., Vacher, H. C., and Bright, H. A., "Cooperative Study of Methods for the Determination of Oxygen in Steel," *J. Research Nat'l Bur. Standards*, 18, No. 3 (1937).

## Appendix III

### Preparation, pH Ranges and Color Changes of Various Organic Chemical Indicators

#### Normality and pH Values

Throughout the methods in this book, and in other chemical work as well, the pH of solutions appears as a most important item in the control of the separation of various elements and compounds.

The pH value refers to the concentration of hydrogen ions in a solution and is stated in terms of the logarithm of the reciprocal of the gram ionic hydrogen equivalent per liter. Mathematically expressed,

$$\text{pH} = \log \frac{1}{(\text{H}^+)} \text{ per liter.}$$

The logarithm of a number is the exponent of that power to which another number, taken as the base, must be raised to obtain the given number. In the common, or Briggian, system the base number is 10, and since most numbers are in commensurable powers of 10, the logarithm of a number consists of an integer, called the characteristic, and an endless decimal, called the mantissa. For example  $258,000,000 = 2.58 \times 10^8$ ,  $\log 8.41162$ , and  $100,000,000 = 1.00 \times 10^8$ ,  $\log 8$ . Also,  $0.1 = 10^{-1}$ ,  $\log 1$  or  $\bar{1}$  and  $.000\ 000\ 001 = 10^{-9}$ ,  $\log -9$  or  $\bar{9}$ .

Normality refers to the hydrogen equivalent of a compound in solution, 1 gram atom of hydrogen per liter being taken as the base.

When an electrolyte, such as an acid, for example, is dissolved in water, the dissociation that takes place to give  $\text{H}^+$  goes to completion only in very dilute solutions. With more concentrated solutions, the hydrogen ion normality is less than the total acid normality and varies for different acids about as follows:

Acid, formula	$\text{HNO}_3$	$\text{HCl}$	$\text{H}_2\text{SO}_4$	$\text{H}_3\text{PO}_4$	$\text{HOOCCH}_3$
Molecular weight and molecules per liter	$63.02 \times 2$	$36.46 \times 2$	$98.08 \times 1$	$98.04 \times \frac{1}{3}$	$60.03 \times 2$
Total acid normality	2	2	2	2	2
Hydrogen ion normality	1.48	1.39	1.01	0.36	0.006

Since hydrogen ion concentration measurements are made on dilute solutions with a normality of 1 or less, pH values represent negative exponents of 10 used as a base to indicate the concentration of hydrogen ions in dilute solutions. These relations are shown in the following table.

TABLE 4. RELATION OF HYDROGEN ION NORMALITY TO pH VALUE

Hydrogen Ion Normality	Hydrogen-Ion Concentrations			
	As indicated by Exponential System	Integral pH System	Numerical Relations Fractional pH Values	Concentration H <sup>+</sup> per liter
1.0	10 <sup>0</sup>	0	<i>N</i> .00	1.00 × 10 <sup>-n</sup>
			.05	8.91 × 10 <sup>-(n+1)</sup>
0.1	10 <sup>-1</sup>	1	.10	7.94
			.15	7.07
0.01	10 <sup>-2</sup>	2	.20	6.31
			.25	5.62
0.001	10 <sup>-3</sup>	3	.30	5.01
			.35	4.46
0.0001	10 <sup>-4</sup>	4	.40	3.98
			.45	3.54
0.00001	10 <sup>-5</sup>	5	.50	3.16
0.000001	10 <sup>-6</sup>	6	.55	2.82
0.0000001	10 <sup>-7</sup>	7	.60	2.51
			.65	2.24
			.70	1.99
0.00000001	10 <sup>-8</sup>	8	.75	1.78
0.000000001	10 <sup>-9</sup>	9	.80	1.58
0.0000000001	10 <sup>-10</sup>	10	.85	1.41
			.90	1.26
			.95	1.12
			( <i>N</i> + 1) .00	1.00

The factors given in the last two columns are used as a convenient means for calculating the actual H<sup>+</sup> concentration from the pH value, as illustrated by the following example.

The pH of a solution = 6.65. Referring to the table, *N* = 6, *N* + 1 = 7, and factor corresponding to *N* .65 = 2.24. Therefore, the H<sup>+</sup> concentration = 2.24 × 10<sup>-7</sup> = 0.000000242.

### Methods for Determining the pH of Solutions

The pH value of solutions is most conveniently determined potentiometrically using the hydrogen electrode, the glass electrode and others, such as the quinhydrone and metal electrodes, which are fully treated in various textbooks on the subject.<sup>1</sup>

Reasonably exact control of the pH of solutions can now be had through the use of proper indicators. The following data, supplied by Eastman Kodak Company, Rochester, New York, have proved useful and are reproduced here as a matter of convenience for reference. All the indicators listed may be obtained from the Eastman Company. The pH values assigned to some indicators by different investigators do not agree exactly. For example, some values obtained by us differ slightly from those in the table, and our findings are given for two indicators by way of illustration. However, for most work these discrepancies are not great enough to be considered seriously.

TABLE 5. PREPARATION OF INDICATOR SOLUTIONS.

Indicator	Suggested Solution
Alizarin Blue S .....	Alcohol
Aurin .....	.04 g in 40 cc alcohol + 60 cc water
Benzeneazodiphenylamine .....	0.01 g in 1 cc NHCl + 50 cc alcohol + 49 cc water
Benzopurpurin 4B .....	0.1 per cent in water
Congo Red.....	0.1 per cent in water
<i>o</i> -Cresolphthalein .....	0.04 per cent in alcohol
Curcumin .....	Alcohol
<i>p</i> -Dimethylaminoazobenzene ....	0.1 g in 90 cc alcohol + 10 cc water
<i>m</i> -Dinitrobenzoyleneurea .....	25 g in 115 cc molar NaOH + 500 cc boiling water, filtered and cooled. .292 g of the salt in 100 cc water
2,4-Dinitrophenol .....	Saturated water solution
2,6-Dinitrophenol .....	0.05 per cent in water
Ethyl Orange .....	0.05-0.2 per cent in water or aqueous alcohol
Lacmoid .....	0.2 per cent in alcohol
Malachite Green .....	Water
Metanil Yellow .....	0.01 per cent in water
Methyl Orange .....	0.01 per cent in water
Methyl Red .....	0.02 g in 60 cc alcohol + 40 cc water
Methyl Violet .....	0.01-0.05 per cent in water
$\alpha$ -Naphtholbenzein .....	1 per cent in dilute alkali
Neutral Red .....	0.01 g in 50 cc alcohol + 50 cc water
<i>m</i> -Nitrophenol .....	0.3 per cent in water
<i>p</i> -Nitrophenol .....	0.1 per cent in water
Orange II .....	0.1 per cent in water
Orange IV .....	0.01 per cent in water
<i>p</i> -Methyl Red .....	Alcohol
Phenolphthalein .....	0.05 g in 50 cc alcohol + 50 cc water
Phenoltetraiodophthalein Sodium Salt .....	Water
Picric Acid.....	Water
Propyl Red .....	Alcohol
Quinaldine Red .....	1 per cent in alcohol
Resazurin .....	Water
Sodium Alizarinsulfonate .....	Dilute solution in water
Sodium 2,4-Dihydroxyazobenzene-4-sulfonate .....	0.01 per cent in water
Sodium Indigodisulfonate .....	Water
Sodium Nitrobenzeneazosalicylate .....	0.01 per cent in water
<i>p</i> -Sulfo- <i>o</i> -methoxybenzeneazodimethyl- $\alpha$ -naphthylamine .....	0.1 per cent in 60 per cent alcohol
Thymolphthalein .....	0.04 g in 50 cc alcohol + 50 cc water
<i>o</i> -Tolueneazo- <i>o</i> -toluidine .....	Water
1,3,5-Trinitrobenzene .....	0.1-0.5 per cent in alcohol
2,4,6-Trinitrotoluene .....	0.1-0.5 per cent in alcohol

Indicators of the sulfonphthalein type are supplied in the acid form. For use, the monosodium salt is prepared and dissolved in water. The general procedure is to grind 0.1 gram of the dry indicator in a mortar with the required amount of alkali and to dilute the mixture

ORGANIC CHEMICAL INDICATORS. (Courtesy Eastman Kodak Company)

Eastman Cat. No.	Chemical Names of Indicator	pH Scale
924	Alpha Naphtholbenzein	0 — 1 — 2 — 3 — 4 — 5 — 6 — 7 — 8 — 9 — 10 — 11 — 12 — 13 — 14
210	Picric Acid	Green — Yellow
1264	Malachite Green	Colorless — Yellow
1309	Methyl Violet	Yellow — Blue Green . Blue
2224	<i>p</i> -Xylenolsulfonphthalein (Xylenol Blue)	Yellow — Blue Violet. — Violet.
1361	Quinadine Red	Pink — Amber
926	<i>p</i> -Methyl Red	Colorless. — Red
1714	Benzenaeodiphenylamine	Red — Yellow
2118	<i>m</i> -Cresolsulfonphthalein ( <i>m</i> -Cresol Purple)	Pink. — Yellow
753	Thyriolsulfonphthalein (Thymol Blue)	Red — Yellow — Purple
T-766	Metanil Yellow	Red — Yellow — Blue
1021	Benzopurpurin 4B	Red — Yellow
P-823	Orange IV (Tropaeolin 00)	Violet — Red
1210	<i>o</i> -Toluenazo- <i>o</i> -Toluidine	Red. — Yellow
		Orange. — Yellow
		0.6 — 2.0*
		1 — 1
744	<i>o</i> -Cresolsulfonphthalein (Cresol Red)	Orange. — Amber — Red
2235	2,6-Dinitrophenol	Colorless. — Yellow
102	2,4-Dinitrophenol	Colorless. — Yellow
338	<i>p</i> -Dimethylaminazo benzene	Red. — Yellow
752	Tetrabromophenolsulfo- phthalein (Brom Phenol Blue)	Yellow. — Blue
770	Congo Red	Blue. — Red.



TABLE 6. (Continued)

Eastman Cat. No.	Chemical and Common Names of Indicator	pH Scale
2757	Tetraiodophenolsulfon- phthalein	0 Yellow 1 Red 2 _____ 3 _____ 4 _____ 5 Yellow 6 _____ 7 Yellow 8 _____ 9 _____ 10 _____ 11 _____ 12 _____ 13 _____ 14 _____
432	Methyl Orange	Red _____ Pink
122	Ethyl Orange	Red _____ Yellow
1954	<i>p</i> -Sulfo- <i>o</i> -Methoxybenzene Azodimethyl- $\alpha$ -Naphthylamine	Red _____ Yellow
1051	Sodium Alizarinsulfonate (Alizarin Red S)	Blue _____ Orange 4.8 _____ 6.8*
1782	Tetrabromo- <i>m</i> -cresolsul- fophthalein (Brom Cresol Green)	Yellow _____ Pink Yellow _____ Blue
2106	Resazurin	Orange _____ Violet
431	Methyl Red	Red _____ Yellow
1750	Lacmoid	Red _____ Blue
944	Propyl Red	Red _____ Yellow
2116	Dichlorophenolsulfonphthalein (Chlor Phenol Red)	Red _____ Yellow
1309	Methyl Violet	Yellow _____ Red
192	<i>p</i> -Nitrophenol	Violet _____ Violet
745	Dibromo- <i>o</i> -cresolsulfon- phthalein (Brom Cresol Purple)	Colorless _____ Yellow
839	Dibromothymolsulfon- phthalein (Brom Thymol Blue)	Yellow _____ Purple
100	<i>m</i> -Dimthbenzoylbenzene	Colorless _____ Blue
783	Aurin (Rosolic Acid)	Amber _____ Yellow
887	Brilliant Yellow	Yellow _____ Pink
755	Neutral Red	Red _____ Orange _____ Amber

TABLE 6. (Continued)

Eastman Cat. No.	Chemical and Common Names of Indicator	pH Scale														
541	Phenolsulfonphthalein (Phenol Red) .....	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1340	<i>m</i> -Nitrophenol .....	Yellow	.....	.....	.....	.....	.....	.....	.....	.....	.....	Red	.....	.....	.....	.....
744	<i>o</i> -Cresolsulfonphthalein (Cresol Red) .....	Colorless	.....	.....	.....	.....	.....	.....	.....	.....	.....	Yellow	.....	.....	.....	.....
2224	<i>p</i> -Xylenolsulfonphthalein (Xylenol Blue) .....	Orange	.....	.....	Amber	.....	.....	.....	.....	.....	.....	Red	.....	.....	.....	.....
1179	Curcumin .....	Pink	.....	.....	Amber	.....	.....	.....	.....	.....	.....	Violet	.....	.....	.....	.....
196	Orange II (Tropaeolin 000) ..	Yellow	.....	.....	.....	.....	.....	.....	.....	.....	.....	Red	.....	.....	Orange	.....
2118	<i>m</i> -Cresolsulfonphthalein ( <i>m</i> -Cresol Purple) .....	Yellow	.....	.....	.....	.....	.....	.....	.....	.....	.....	Amber	.....	.....	Red	.....
753	Thymolsulfonphthalein (Thymol Blue) .....	Red	.....	.....	.....	Yellow	.....	.....	.....	.....	.....	Purple	.....	.....	.....	.....
924	Alpha Naphtholbenzein .....	Red	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Blue	.....	.....	.....
774	<i>o</i> -Cresolphthalein .....	Colorless—Yellow	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Blue Green	.....	.....
2214	Phenol Tetraiodophthalein Sodium Salt .....	Colorless	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Red	.....
202	Phenolphthalein .....	Colorless	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Pink	.....
1091	Thymolphthalein .....	Colorless	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Pink	.....
784	Sodium Nitrobenzenazo- salicylate (Alizarin Yel- low R) .....	Colorless	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Blue
1759	Alizarin Blue S .....	Yellow	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Red
1992	Sodium 2,4-Dihydroxyazo- zene-4-Sulfonate Tropaeolin 0 .....	Amber	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Yellow Green, Green, — Blue Green
P-1009	Sodium Indigodisulfonate ..	Yellow	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Orange
1264	Malachite Green .....	Blue	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Yellow
268	2,4,6-Trinitrotoluene .....	Colorless	.....	.....	.....	Blue Green	.....	.....	.....	.....	.....	.....	.....	.....	.....	Colorless
639	1,3,5-Trinitrobenzene .....	Colorless	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Orange

\* Checked by H. J. Walthorn.

to 250 cc which gives a strength of 0.04 per cent. In the following table, the figures given are the number of cubic centimeters of 0.01 *N* sodium hydroxide required to form the monosodium salt.

<i>o</i> -Cresolsulfonphthalein (Cresol Red) .....	26.2
<i>m</i> -Cresolsulfonphthalein ( <i>m</i> -Cresol Purple) .....	26.2
Dibromo- <i>o</i> -cresolsulfonphthalein (Bromcresol Purple) .....	18.5
Dibromothymolsulfonphthalein (Bromthymol Blue) .....	16.0
Dichlorophenolsulfonphthalein (Chlorphenol Red) .....	23.6
Phenolsulfonphthalein (Phenol Red) .....	28.2
Tetrabromo <i>m</i> -Cresolsulfonphthalein (Bromcresol Green)....	14.3
Tetrabromophenolsulfonphthalein (Bromphenol Blue) .....	14.9
Tetraiodophenolsulfonphthalein .....	11.7
Thymolsulfonphthalein (Thymol Blue) .....	21.5
<i>p</i> -Xylenolsulfonphthalein (Xylenol Blue) .....	24.4

### Notes on Indicators

1. From the preceding table, it is apparent that there are few indicators which change color at the neutral point pH 7. Those that change at pH > 7 are classed as acid-sensitive, while those that change at pH < 7 are classed as base-sensitive.

2. CO<sub>2</sub> must be excluded from titrations with acid-sensitive indicators.

3. As a rule, one-color indicators are affected by the concentration. For example, a very dilute solution of phenolphthalein may show a faint color at pH 9, while a more concentrated solution may show the same color at pH 8.

4. Indicators are also affected by the temperature of the titrating solution, the concentration of neutral salts, the presence of alcohol, and proteins.

5. Some indicators, such as methyl red, cannot be used in the presence of oxidizing solutions, and some, like alizarin, cannot be used in the presence of aluminum, as they form a lake with Al(OH)<sub>3</sub>.

6. Some substances, called buffers, such as potassium chloride, acid potassium phthalate, acid potassium phosphate, sodium borate, resist a change in pH and affect some indicators.

Indicators suitable for titrating a few different substances are shown in the following table.

### Text Reference

- , I. M., and Furman, N. H., "Potentiometric Titrations," New York, John Wiley 1931.

TABLE 7. INDICATORS SUITABLE FOR TITRATING VARIOUS SUBSTANCES

Substance	Indicator
Acids, strong, nonoxidizing, mineral $\text{HCl}$ , $\text{H}_2\text{SO}_4$	Any indicator
strong oxidizing $\text{HNO}_3$	All except those affected by oxidizing agents
Ammonia	Bromphenol Blue, Bromeresol Purple, Methyl Orange, Methyl Red, Methyl Yellow
Monobasic	Bromphenol Blue, Methyl Orange, Methyl Yellow
Arsenic Acid    Dibasic, solution saturated with $\text{NaCl}$	Thymolphthalein, Thymol Blue, and Phenolphthalein
Tribasic, presence of much $\text{CaCl}_2$	Phenolphthalein, Thymol Blue
Arsenious Acid (Monobasic only)	
Bases, strong, $\text{NaOH}$ , $\text{KOH}$	Any indicator
Benzoic Acid	Phenolphthalein and Thymol Blue
Boric Acid	Nitramin Tropaeolin 0
Boric Acid + polybasic alcohols (mannite or glycerine)	Phenolphthalein, Thymol Blue
Carbonic Acid    { Monobasic + $\text{NaCl}$	Phenolphthalein, Thymol Blue
{ Dibasic + $\text{BaCl}_2$	Phenolphthalein, Thymol Blue
(Titrated with strong base)	
Chromic Acid (Titrated with strong base)	Phenolphthalein, Thymol Blue
Formic Acid	Phenolphthalein, Thymol Blue, Phenol Red, Neutral Red
Hydrofluoric Acid	Phenolphthalein, Thymol Blue, Phenol Red, Neutral Red
Hydrocyanic Acid	Nitramin, Tropaeolin 0
Oxalic Acid	Phenolphthalein, Thymol Blue, Phenol Red, Neutral Red

## Appendix IV

Table of Atomic Weights, Atomic Numbers, and Other  
Physical Constants of the Chemical Elements

TABLE 8. PHYSICAL AND CHEMICAL CONSTANTS OF THE ELEMENTS IN ALPHABETICAL ORDER, INCLUDING SPECTROGRAPHIC AND X-RAY DATA

Name of Element	Sym- bol	Atomic Number*	Inter- national <sup>1</sup> Atomic Wts.	Logarithm	Valence	Density	Melting Point (°C)	Boiling Point (°C)	Crystal System**	Unit Cell Size Angstrom Units $a$	Wave Length K $\alpha$ in A.U.
Actinium*	Ac	89	228.0		3	1800	Discovery in doubt		Fe	4.0406	8.3205
Alabamine*	Ab (?)	85	221.0		8		659.7	1800		4.5; 56° 37'	0.47387
Aluminum	Al	13	26.97	1.43088	3	2.70	660.5	1440	Rh	4.0406	0.47387
Antimony	Sb	51	121.76	2.08554	3.5	6.68	180.6	186.1	Fe	5.43	1.17743
Argon	Ar	18	39.944	1.60141	0	1.65	820	6158	Rh	4.142; 54° 7'	0.38899
Arsenic	As	33	74.91	1.87483	3.5	5.73	850	960	Bc	2.968	115.7
Barium	Ba	56	137.36	2.13789	2	3.5	1350		Hc	4.726; 57° 16'	0.16525
Beryllium	Be	4	9.02	0.95621	2	1.85	271.3	1436	Rh		67.71
Bismuth	Bi	83	209.00	2.32015	3.5	9.78	2300	2500	H		1.04166
Boron	B	5	10.82	1.03423	3	2.0	—7.2	61.1	R	2.98	0.53832
Bromine	Br	35	79.916	1.90264	1.3, 5.7	(3.4)	320.9	778	Hc	5.56	3.35495
Cadmium	Cd	48	112.41	2.05081	2	8.64	810		Fe		
Calcium	Ca	20	40.08	1.60282	2	1.55	850		amorph.		
Carbon	C	6	12.01	1.07918	2, 4	1.88	3500		Te	3.56	44.54
Diamond						3.51			H	2.46	
Graphite						2.25			Fe	5.143	
Cerium	Ce	58	140.13	2.14601	3, 4	6.90	640		Bc		0.36110
Cesium	Cs	55	132.81	2.12323	1	1.90	26	670	R		0.40411
Chlorine	Cl	17	35.457	1.54970	1.3, 5.7	(1.9)	—40	—33.6	Bc	2.8787	4.7212
Chromium	Cr	24	52.01	1.71609	2.3, 6	7.1	1615	2200	Fe	3.554	2.28891
Cobalt	Co	27	58.94	1.77041	2.3	8.9	1480		Bc	3.294	1.78919
Columbium	Cb	41	92.91	1.96895	2.3, 4.5	8.4	1950		Bc	3.6077	0.74889
Copper	Cu	29	63.57	1.80325	1.2	8.93	1083	2310	Fe		1.541232
Dysprosium	Dy	66	162.46	2.21060	3		1250				0.27375
Erbium	Er	68	167.64	2.22453	3	4.77					0.25664
Europium	Eu	63	152.0	2.18184	3	(1.3)	—223	—187			0.30265
Fluorine	F	9	19.00	1.27875	1				O	4.506	18.275
Gadolinium	Gd	64	156.9	2.19662	3	5.91	30.1		Te	4.506	0.29261
Gallium	Ga	31	69.72	1.84336	3	5.36	958	1350	Fe	5.62	1.34087
Germanium	Ge	32	72.60	1.86094	4	5.36	1063	2500	Hc	4.936	1.25521
Gold	Au	79	197.2	2.29491	1.3	19.32	1700			3.32	0.18483
Hafnium	Hf	72	178.6	2.25188	4	13.3					0.22663



TABLE 8. (Continued)

Name of Element	Sym- bol	Atomic Number <sup>1</sup>	1937 Inter- national Atomic Wts.	Logarithm	Valence	Density	Melting Point (°C)	Boiling Point (°C)	Crystal System**	Unit Cell Size Angstrom Units $a$	Wave Length $K\alpha$ in A.U. $c$
Ruthenium	Ru	44	101.7	2.00732	3, 4, 6, 8	12.2	2450			2.686	0.64606
Samarium	Sm	62	150.43	2.17734	3	7.7	1350		He	4.272	0.31302
Scandium	Sc	21	45.10	1.65418	3	(2.5)	1200				3.0284
Selenium	Se	34	78.96	1.89873	2, 4, 6	4.50	217	690	M	8.992	1.10652
Silicon	Si	14	28.06	1.44809	4	2.42	1420	690	Tc	5.42	7.1106
Silver	Ag	47	107.880	2.03294	1	10.5	960.5	1955	Fe	4.0772	0.56267
Sodium	Na	11	22.997	1.36167	1	.97	97.5	880	Bc	4.30	11.885
Strontium	Sr	38	87.63	1.94265	2	2.6	900		Fe	6.075	0.87761
Sulphur	S	16	32.06	1.50602		2.07	112.8		Re	10.61	5.3637
Tantalum	Ta	73	180.88	2.25888	2, 4, 6	16.6	2910	444.7	M	26.4	
Tellurium	Te	52	127.61	2.10551	5	6.24	451	1390	Bc	3.296	0.21973
Terbium	Tb	65	159.2	2.20194	2, 4, 6				H	4.44	0.45491
Thallium	Tl	81	204.39	2.31046	1, 3	11.85	301.7	1280	He	3.47	0.28286
Thorium	Th	90	232.12	2.36577	4	11.5	1842		Fe	5.04	0.17466
Thulium	Tm	69	169.4	2.22891	3						0.1368
Tin	Sn	50	118.70	2.07445	2, 4	7.31	231.9	2270	Bt	5.8194	0.24861
Titanium	Ti	22	47.90	1.68034	3, 4	4.5	1850		He	3.1753	0.49402
Tungsten	W	74	184.0	2.26482	2, 4, 6	19.1	3400		Bc	2.92	2.74681
Uranium	U	92	238.07	2.37689	4, 6	18.7	1690		M	3.1589	0.21337
Vanadium	V	23	50.95	1.70723	3, 5	5.96	1780		Bc	2.829	0.13095
Virginium***	Vi(?)	87	222.5		1	Discovery in doubt				3.04	2.50213
Xenon	Xe	54	131.3	2.11461	0	(2.7)	-140	-109.1	Fe	6.24; 88° K	0.417
Ytterbium	Yb	70	173.04	2.23955	3		1800				0.24098
Yttrium	Y	39	88.92	1.94900	3	5.51	1490	2500	He	3.66	0.83132
Zinc	Zn	30	65.38	1.81544	2	7.14	419.4	930	He	2.6589	1.43603
Zirconium	Zr	40	91.22	1.96009	4	6.4	2350		Bc	3.61	0.78851

<sup>1</sup> The international atomic weights are referred to weightings in vacuo.

For most of the elements, the weights in air, which can be calculated from the weights in vacuo, the atomic volumes, and the buoyant effect of air (equal to the weight of air displaced), are slightly less than the weight in vacuo. As the difference, if any, extends only to the second and third decimal places, it is ignored in ordinary analytical work.

\*\* Legend—Crystal System Abbreviations.  
in doubt, are not listed in the 1937 Table of International Atomic Weights. Hence different names may be applied to them. For example, masurium is also known as eka-manganese.





**General References**

Journal of the American Chemical Society, Industrial and Engineering Chemistry.  
International Critical Tables.  
The Journal of Research of the National Bureau of Standards.  
Current literature, private communications, and public lectures.